

Organization **TC1700** Bldg./Room **REMPSEN**
U. S. DEPARTMENT OF COMMERCE
COMMISSIONER FOR PATENTS

P.O. BOX 1450

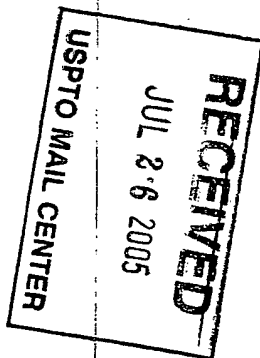
ALEXANDRIA, VA 22313-1450

IF UNDELIVERABLE RETURN IN TEN DAYS

OFFICIAL BUSINESS

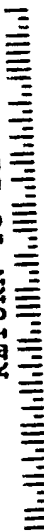
AN EQUAL OPPORTUNITY EMPLOYER

U.S. OFFICIAL MAIL
PENALTY FOR
PRIVATE USE \$300
02 1A
0004204479
MAILED FROM ZIP CODE 22313



RESE008 123013030 1604 17 07/22/05
FORWARD TIME EXP RTN TO SEND
:GE CORP RESEARCH & DEVELOPMENT
1 RESEARCH CIR
SCHENECTADY NY 12309-1027

RETURN TO SENDER



Best Available Copy



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

Ifw

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/644,103	05/14/2004	Anant Achyut Setlur	RD-29215	6488

7590 07/19/2005

General Electric Company
CRD Patent Docket Rm 4A59
P.O. Box 8, Bldg. K-1
Schenectady, NY 12301

EXAMINER

KOSLOW, CAROL M

ART UNIT PAPER NUMBER

1755

DATE MAILED: 07/19/2005

Please find below and/or attached an Office communication concerning this application or proceeding.

RECEIVED
OIP/ELAP
JUL 26 2005

Office Action Summary

Application No.

10/644,103

Applicant(s)

SETLUR ET AL.

Examiner

C. Melissa Koslow

Art Unit

1755

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☐ Responsive to communication(s) filed on ____.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-34 is/are pending in the application.
- 4a) Of the above claim(s) ____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) ____ is/are allowed.
- 6) ☒ Claim(s) 1-34 is/are rejected.
- 7) ☒ Claim(s) 4 is/are objected to.
- 8) ☐ Claim(s) ____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☒ The specification is objected to by the Examiner.
- 10) ☒ The drawing(s) filed on 5/14/05 is/are: a) ☐ accepted or b) ☒ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. ____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- * See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)
Paper No(s)/Mail Date 5/14/04.
- 4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. ____.
- 5) ☐ Notice of Informal Patent Application (PTO-152)
- 6) ☐ Other: ____.

The numbering of claims is not in accordance with 37 CFR 1.126 which requires the original numbering of the claims to be preserved throughout the prosecution. When claims are canceled, the remaining claims must not be renumbered. When new claims are presented, they must be numbered consecutively beginning with the number next following the highest numbered claims previously presented (whether entered or not).

Misnumbered claims 25-32 been renumbered 27-32.

The subject matter of line 23 on page 22 through line 2 on page 23 is a claim which has been numbered claim 25.

The subject matter of lines 3-4 on page 23 is a claim which has been numbered claim 26.

The drawings are objected to as failing to comply with 37 CFR 1.84(p)(5) because they do not include the following reference sign(s) mentioned in the description: #352 in paragraph [0058] is not on fig. 7. Corrected drawing sheets in compliance with 37 CFR 1.121(d) are required in reply to the Office action to avoid abandonment of the application. Any amended replacement drawing sheet should include all of the figures appearing on the immediate prior version of the sheet, even if only one figure is being amended. Each drawing sheet submitted after the filing date of an application must be labeled in the top margin as either "Replacement Sheet" or "New Sheet" pursuant to 37 CFR 1.121(d). If the changes are not accepted by the examiner, the applicant will be notified and informed of any required corrective action in the next Office action. The objection to the drawings will not be held in abeyance.

The drawings are objected to as failing to comply with 37 CFR 1.84(p)(5) because they include the following reference character(s) not mentioned in the description: # 220 in fig 6. Corrected drawing sheets in compliance with 37 CFR 1.121(d), or amendment to the

Art Unit: 1755

specification to add the reference character(s) in the description in compliance with 37 CFR 1.121(b) are required in reply to the Office action to avoid abandonment of the application. Any amended replacement drawing sheet should include all of the figures appearing on the immediate prior version of the sheet, even if only one figure is being amended. Each drawing sheet submitted after the filing date of an application must be labeled in the top margin as either "Replacement Sheet" or "New Sheet" pursuant to 37 CFR 1.121(d). If the changes are not accepted by the examiner, the applicant will be notified and informed of any required corrective action in the next Office action. The objection to the drawings will not be held in abeyance.

The disclosure is objected to because of the following informalities: There are no degree symbols in the specification. Applicants need to clarify if all the elements listed in the parenthesis of formulas, where there is no subscript, need be present or if only at least one need be present. In the art, both interpretations are applicable. Thus, applicants need to make clear their interpretation of these formulas. Appropriate correction is required.

The specification is objected to as failing to provide proper antecedent basis for the claimed subject matter. See 37 CFR 1.75(d)(1) and MPEP § 608.01(o). Correction of the following is required: The subject matter of claim 28, a radiation source that emits radiation in the wavelength range of about 250 nm to about 420 nm, is not found in the specification.

Claims 6, 10 and 20 are objected to because of the following informalities: The degree symbols are missing from these claims. Appropriate correction is required.

Claim 2 is rejected under 35 U.S.C. 112, first paragraph, as containing subject matter which was not described in the specification in such a way as to reasonably convey to one skilled

Art Unit: 1755

in the relevant art that the inventors, at the time the application was filed, had possession of the claimed invention.

Claim 20 teaches the amount of europium is about 10-40 at%, based on the combined amount of A and europium ions, while paragraphs [0020] and [0022] teach the amount of europium is about 10-50 at%, preferably about 20-40 at%, based on the combined amount of A and europium ions. The discrepancies between the claimed range and the ranges in the specification need to be corrected.

Claims 23, 24, 26, 31, 32 and 34 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

In claims 23 and 24, applicants need to clarify if all the elements listed in the parenthesis of formulas, where there is no subscript, need be present or if only at least one need be present. In the art, both interpretations are applicable. Thus, applicants need to make clear their interpretation of these formulas. Claims 26, 31 and 32 are all improperly dependent on claim 24. Claim 24 is directed to a phosphor blend, not a light source. Claims 26 and 31 should be dependent on claim 25. Claim 32 should be dependent on claim 31 since this is the teaching in the claims of gas discharge devices. Claim 34 is also improperly dependent on claim 24. It is noted that paragraph [0059] teaches the phosphor of claim 1 can be used in cathode-ray tubes and there is no teaching of the use of a cathode ray tube as a radiation source that emits wavelengths in the range of about 250-480 nm.

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

Art Unit: 1755

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

(e) the invention was described in (1) an application for patent, published under section 122(b), by another filed in the United States before the invention by the applicant for patent or (2) a patent granted on an application for patent by another filed in the United States before the invention by the applicant for patent, except that an international application filed under the treaty defined in section 351(a) shall have the effects for purposes of this subsection of an application filed in the United States only if the international application designated the United States and was published under Article 21(2) of such treaty in the English language.

Claims 6, 7, 10, 11, 13, 25, 31 and 33 are rejected under 35 U.S.C. 102(b) as being clearly anticipated by JP 2000-109826.

This reference teaches a fluorescent lamp comprising a phosphor having the formula $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$, where x is 0.4-0.6, y is 0.03-0.3 and z is 0-0.04. The phosphor is produced by mixing carbonates of barium, strontium and magnesium; europium oxide; manganese oxide, magnesium hydroxide, alumina and aluminum fluoride flux and firing the mixture at 1200-1700°C in a reducing atmosphere for 2-40 hours. The examples teach a firing temperature of 1450°C, a firing time of 24 hours and an atmosphere is a blend of nitrogen and hydrogen. The y values in the examples 0.1 and the z range values are 0.008-0.025. These values fall within the range of claim 6. The taught phosphor is blended with a red and green phosphor and used in a fluorescent lamp, which is known in the art to comprise a gas discharge device that emits ultraviolet radiation of about 250 nm. The reference teaches the claimed process and device.

Claims 6, 7, 10, 11, 13, 25, 31 and 33 are rejected under 35 U.S.C. 102(b) as being clearly anticipated by JP 08-283712.

This reference teaches a fluorescent lamp comprising a phosphor having the formula $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$, where x is 0.1-0.4, y is 0.075-0.4 and z is 0.005-0.05. The phosphor is produced by mixing carbonates of barium, strontium and magnesium; europium

Art Unit: 1755

oxide; manganese oxide, magnesium hydroxide, alumina and aluminum fluoride flux and firing the mixture at 1200-1700°C in a reducing atmosphere for 2-40 hours. The examples teach a firing temperature of 1450°C, a firing time of 24 hours and an atmosphere is a blend of nitrogen and hydrogen. The y values in the examples 0.1 and the z range values are 0.012-0.02. These values fall within the range of claim 6. The taught phosphor is blended with a red and green phosphor and used in a fluorescent lamp, which is known in the art to comprise a gas discharge device that emits ultraviolet radiation of about 250 nm. The reference teaches the claimed process and device.

Claims 1, 22, 23 and 25-29 are rejected under 35 U.S.C. 102(e) as being anticipated by U.S. patent 6,805,600 and are rejected under 35 U.S.C. 102(b) as being anticipated by U.S. published patent application 2003/0075705.

U.S. published patent application 2003/0075705 was issued as U.S. patent 6,805,600.

These references teach a phosphor having the formula $\text{Ba}_{0.9}\text{Eu}_{0.1}\text{Mg}_{0.93}\text{Mn}_{0.07}\text{Al}_{10}\text{O}_{17}$. This formula falls within that of claim 1. This phosphor is blended with a red phosphor or orange red phosphor. The reference exemplifies blends of $\text{Ba}_{0.9}\text{Eu}_{0.1}\text{Mg}_{0.93}\text{Mn}_{0.07}\text{Al}_{10}\text{O}_{17}$ and $\text{Y}_2\text{O}_3:\text{Eu}$, one of the phosphors of claim 23. This blend is deposited adjacent to a UV/blue light emitting diode, preferably a 396 nm emitting LED. The reference teach the device can be in the formula of a lamp, which has the standard structure where the phosphor blend is dispersed in a transparent casting disposed adjacent to the LED. The references teach the claimed phosphor, blend and device.

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

Art Unit: 1755

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 1, 6, 7, 10-13, 22, 23, 25, 31-33 are rejected under 35 U.S.C. 103(a) as being unpatentable over JP 2000-109826.

As stated above, this reference teaches producing phosphor having the formula $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$, where x is 0.4-0.6, y is 0.03-0.3 and z is 0-0.04. The taught y and z values overlap the claimed range since 0.04 falls within the scope of the claimed value of "about 0.05". Product claims with numerical ranges which overlap prior art ranges were held to have been obvious under 35 USC 103. *In re Wertheim* 191 USPQ 90 (CCPA 1976); *In re Malagari* 182 USPQ 549 (CCPA 1974); *In re Fields* 134 USPQ 242 (CCPA 1962); *In re Nehrenberg* 126 USPQ 383 (CCPA 1960). The phosphor is produced by mixing oxides or compounds which generate oxides of Ba, Sr, Mn, Mg, Eu and Al and aluminum fluoride flux and firing the mixture at 1200-1700°C in a reducing atmosphere for 2-40 hours. The examples teach the atmosphere is a blend of nitrogen and hydrogen. The taught time and temperature ranges overlap those claimed. From the examples, one of ordinary skill in the art would have found it obvious to use a mixture of carbonates and oxides as the sources of the elements used in the process. The taught phosphor is blended with a red and green phosphor and used in a fluorescent lamp, which is known in the art to comprise a gas discharge device that emits ultraviolet radiation of about 250 nm. While the reference does not teach the type of lamps, it is well known that the most conventional type of fluorescent lamp are mercury gas lamps. Thus, one of ordinary skill in the art would have found it obvious to use a mercury gas lamp as the taught lamps. The taught red phosphor is

Art Unit: 1755

$\text{Y}_2\text{O}_3\text{:Eu}$ and the green phosphor $\text{LaPO}_4\text{:Ce,Tb}$, two of the phosphors of claim 23. The reference suggests the claimed phosphor, blend and device.

Claims 1, 6, 7, 10-13, 22, 23, 25, 31-33 are rejected under 35 U.S.C. 103(a) as being unpatentable over JP 2000-109826.

As stated above, this reference teaches producing phosphor having the formula $\text{Ba}_{1-x-y}\text{Sr}_x\text{Eu}_y\text{Mg}_{1-z}\text{Mn}_z\text{Al}_{10}\text{O}_{17}$, where x is 0.1-0.4, y is 0.075-0.4 and z is 0.005-0.05. The taught y and z values overlap the claimed ranges. Product claims with numerical ranges which overlap prior art ranges were held to have been obvious under 35 USC 103. *In re Wertheim* 191 USPQ 90 (CCPA 1976); *In re Malagari* 182 USPQ 549 (CCPA 1974); *In re Fields* 134 USPQ 242 (CCPA 1962); *In re Nehrenberg* 126 USPQ 383 (CCPA 1960). The phosphor is produced by mixing oxides or compounds which generate oxides of Ba, Sr, Mn, Mg, Eu and Al and aluminum fluoride flux and firing the mixture at 1200-1700°C in a reducing atmosphere for 2-40 hours. The examples teach the atmosphere is a blend of nitrogen and hydrogen. The taught time and temperature ranges overlap those claimed. From the examples, one of ordinary skill in the art would have found it obvious to use a mixture of carbonates and oxides as the sources of the elements used in the process. The taught phosphor is blended with a red and green phosphor and used in a fluorescent lamp, which is known in the art to comprise a gas discharge device that emits ultraviolet radiation of about 250 nm. While the reference does not teach the type of lamps, it is well known that the most conventional type of fluorescent lamp are mercury gas lamps. Thus one of ordinary skill in the art would have found it obvious to use a mercury gas lamp as the taught lamps. The taught red phosphor is $\text{Y}_2\text{O}_3\text{:Eu}$ and the green phosphor

Art Unit: 1755

$\text{LaPO}_4\text{:Ce,Tb}$, two of the phosphors of claim 23. The reference suggests the claimed phosphor, blend and device.

Claims 1, 3, 14, 22, 23 and 25-29 are rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. patent 6,805,600 or U.S. published patent application 2003/0075705.

These reference teach a phosphor having the formula $(\text{Ba}_{1-x}\text{Eu}_x)(\text{Mg}_{1-y}\text{Mn}_y)\text{Al}_{10}\text{O}_{17}$, where $0 < x \leq 0.5$ and $0 < y \leq 0.5$. These values of x and y overlap the claimed amounts of europium and manganese. The references teach the phosphor can be produced by a co-precipitation process, which is known in the art to comprise providing a first solution containing ions of barium, magnesium, europium, manganese and aluminum, adding a second solution which causes the metal ions to precipitate a compound that will form an oxide upon firing and firing the mixture under a reducing atmosphere at a time and temperature to form the phosphor. As discussed above, the references teach blending this phosphor with a red or orange-red phosphor, such as $\text{Y}_2\text{O}_3\text{:Eu}$. The reference teaches the device where the phosphor blend is disposed adjacent to a UV emitting LED, such as a 396 nm LED can be in the form of a lamp. These lamps are known to have the structure where the phosphor blend is dispersed in a transparent casting which is disposed adjacent to the LED. The references suggest the claimed phosphor, process, blend and device.

Claim 30 is rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. patent 6,805,600 or U.S. published application 2003/0075705 as applied to claim 29 above, and further in view of U.S. patent 6,252,254.

As discussed above, U.S. patent 6,805,600 and U.S. published application 2003/0075705 teach lamps comprising a UV LED and a blend of a phosphor having the formula $(\text{Ba}_1$.

Art Unit: 1755

$x\text{Eu}_x)(\text{Mg}_{1-y}\text{Mn}_y)\text{Al}_{10}\text{O}_{17}$, where $0 < x \leq 0.5$ and $0 < y \leq 0.5$ and a red or orange-red phosphor. U.S. patent 6,252,254 shows the standard structure of these lamps, which reads upon that of claim 27. Column 7, lines 11-22 teaches that these lamps can contain scattering particles also dispersed in the transparent casting to reduce the optical saturation effects and to reduce physical damage of the phosphor. Therefore, one of ordinary skill in the art would have found it obvious to include scattering particles in the lamps of U.S. patent 6,805,600 and U.S. published application 2003/0075705 to reduce the optical saturation effects and to reduce physical damage of the phosphor. The references suggest the claimed device.

Claims 15 and 16 are rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. patent 6,805,600 or U.S. published application 2003/0075705 as applied to claim 14 above, and further in view of U.S. patent 6,685,852.

As discussed above, U.S. patent 6,805,600 and U.S. published application 2003/0075705 teach forming the phosphor through co-precipitation, which is known in the art to comprise providing a first solution containing ions of barium, magnesium, europium, manganese and aluminum, adding a second solution which causes the metal ions to precipitate a compound that will form an oxide upon firing and firing the mixture under a reducing atmosphere at a time and temperature to form the phosphor. These references do not give any details of this process, such as what anions in the second solution can be used to precipitate compounds of Ba, Mg, Eu, Mn and Al. U.S. patent 6,685,852 teaches forming aluminate phosphors comprising Ba, Mg, Eu, Mn and Al by co-precipitation, where the second solution comprises ammonium hydroxide or organic amines (col. 4, lines 59-66). One of ordinary skill in the art would have found it obvious to use the ammonium hydroxide or organic amine solution as the precipitating solution in the

Art Unit: 1755

process of U.S. patent 6,805,600 and U.S. published application 2003/0075705. The references suggest the claimed process.

Claims 1-3 and 14-30 are rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. patent 6,685,852.

Applicant has provided evidence in this file showing that the invention was owned by, or subject to an obligation of assignment to, the same entity as U.S. patent 6,685,852 at the time this invention was made, or was subject to a joint research agreement at the time this invention was made. However, the reference additionally qualifies as prior art under another subsection of 35 U.S.C. 102, and therefore, is not disqualified as prior art under 35 U.S.C. 103(c).

Applicant may overcome the applied art either by a showing under 37 CFR 1.132 that the invention disclosed therein was derived from the invention of this application, and is therefore, not the invention "by another," or by antedating the applied art under 37 CFR 1.131.

This reference teaches a light source comprising a UV/blue light LED which emits wavelengths in the range of 350-400 nm as the radiation source and a transparent casting adjacent to the LED comprising scattering particles a blend of at least two phosphors, where one phosphor has the formula $(\text{Ba}, \text{Sr}, \text{Ca})\text{MgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}, \text{Mn}^{2+}$ and the other can be one of the phosphors of claim 24, which emit yellow, blue or blue-green. Column 4, lines 1-5 teaches that this phosphor actual has the formula $\text{AMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}, \text{Mn}^{2+}$, where A is at least one of Ba, Ca and Sr and that the amount of europium is less than 20% of the total amount of A and europium and that the amount of manganese is less than 20% of the total amount of magnesium and manganese. The taught amounts of europium and manganese overlap those claimed. Thus the reference suggests the compositions of claims 1-3. The reference teaches the phosphor are

Art Unit: 1755

produced by a co-precipitation process where a first solution comprising the desired metals are combined with a second solution containing ammonium hydroxide or organic amines to precipitate compounds of the metals that can be converted to the phosphor upon heating in a reducing atmosphere at a temperature greater than 900°C for a time sufficient to produce the phosphor. These temperature and time ranges overlap the claimed ranges. While the reference does not teach the composition of the reducing atmosphere, one of ordinary skill in the art would have found it obvious to use any well known reducing atmosphere, such as the combination of nitrogen and hydrogen, the product of an incomplete combustion of carbon in air or a hydrazine atmosphere. The reference suggests the claimed device, blend, process and phosphor.

Claims 1-3, 5-8, 10-13, 25 and 31 rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. patent 5,611,959.

This reference teaches phosphors used in rare gas discharge lamps. These lamps are known to have a gas discharge device as a radiation source that emits radiation in the range of about 250-480 nm. The phosphor has the formula $(M_{1-x}Eu_x)O^*a(M'_{1-y}Mn_y)^*(5.5-5a)Al_2O_3$, where $0 < a \leq 2$, x is 0.1-0.5, y is 0-0.2. M is Sr and at least one of Ca or Ba and M' is Mg and/or Zn. The examples show that a is preferably 1. Thus the reference suggests a phosphor with the formula $MM'Al_{10}O_{17}$, where M is Sr and at least one of Ca or Ba, x is 0.1-0.5, y is 0-0.2 and M' is Mg and/or Zn, which suggests that both Mg and Zn are present, where the amount of zinc is greater than 0 up to less than 100 at% of the total amount of Zn, Mg and Mn. This formula overlaps those claimed. The reference teaches that the phosphor is produced by combining oxides or carbonates of the required metals with a flux selected from fluorides of magnesium, barium or aluminum and firing this mixture in a reducing atmosphere at 1200-1700°C for 2-40

Art Unit: 1755

hours. The claimed temperature and time ranges overlaps those claimed. The taught atmosphere can be a mixture of nitrogen and hydrogen or the product of an incomplete combustion of carbon in air. The reference suggests the claimed phosphor, process and device.

Claim 9 is rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. patent 5,611,959 as applied to claim 6 above, and further in view of U.S. patent 5,735,921.

U.S. patent 5,611,959 teaches the use of any reducing atmosphere in the taught process. It does not teach the use of ammonia or hydrazine. U.S. patent 5,735,921 teaches the use of hydrazine will produce a reducing atmosphere that is functionally equivalent to hydrogen and carbon monoxide atmospheres taught in U.S. patent 5,611,959. Thus, one of ordinary skill in the art would have found it obvious to use a hydrazine atmosphere as the reducing atmosphere of U.S. patent 5,611,959. The reference suggests the claimed process.

Claims 1, 3 and 5 are rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. patent 6,096,243.

Column 4, lines 5-9 teaches a phosphor having the formula $(\text{Ba}_{1-b-c-d}\text{Sr}_b\text{Ca}_c\text{Eu}_d)(\text{Mg}_{1-f-g}\text{Zn}_f\text{Mn}_g)\text{Al}_{10}\text{O}_{17}$, where $0 \leq b < 1$, $0 \leq c < 1$, $0 \leq f < 1$, $0 \leq g < 1$ and $0 < d < 1$. This composition overlaps the claimed formula. The reference suggests the claimed phosphor.

Claim 4 is objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

There is no teaching or suggestion in the cited art of record of the claimed phosphor.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Melissa Koslow whose telephone number is (571) 272-1371. The examiner can normally be reached on Monday-Friday from 8:00 AM to 3:30 PM.


Art Unit: 1755

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Jerry Lorengo, can be reached at (571) 272-1233.

The fax number for all official communications is (571) 273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

cmk
July 15, 2005


C. Melissa Koslow
Primary Examiner
Tech. Center 1700

FORM PTO-1449
(REV. 7-80)
(Title Amended 3/83)

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

ATTY. DOCKET NO.

RD-29215

SERIAL NO.

101644103

INFORMATION DISCLOSURE STATEMENT BY APPLICANT--
LIST OF ITEMS

(Use several sheets if necessary)

Applicant

A. A. Setlur et al.

Filing Date

Group

U.S. PATENT DOCUMENTS

*EXAMINER INITIAL	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE
9	AA 6 5 6 5 7 7 1	05/20/03	Ono et al.			
	AB 5 7 7 7 3 5 0	07/07/98	Nakamura et al.			
	AC 5 9 9 8 9 2 5	12/07/99	Shimizu et al.			
	AD					
	AE					
	AF					
	AG					
	AH					
	AI					
	AJ					
	AK					

FOREIGN PATENT DOCUMENTS

	DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION	
						YES	No
	AL						
	AM						
	AN						
	AO						
	AP						

OTHER INFORMATION (Including Author, Title, Date, Pertinent pages. Etc)

6	AR	S. Shionoya and W.M. Yen (ed.), "Phosphors Handbook", pp. 389-394, 416-419, CRC Press, Boca Raton (1999)
	AS	
	AT	

EXAMINER

DATE CONSIDERED

7/28/05

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Notice of References Cited	Application/Control No. 10/644,103	Applicant(s)/Patent Under Reexamination SETLUR ET AL.	
	Examiner C. Melissa Koslow	Art Unit 1755	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
	A	US-2003/0075705	04-2003	Wang et al.	252/301.40P
	B	US-6,805,600 B2	10-2004	Wang et al.	445/24
	C	US-6,685,852 B2	02-2004	Setlur et al.	252/301.4R
	D	US-6,252,254 B1	06-2001	Soules et al.	257/89
	E	US-6,096,243 A	08-2000	Oshio et al.	252/301.4R
	F	US-5,735,921	04-1998	Araujo et al.	65/32.1
	G	US-5,611,959 A	03-1997	Kijima et al.	252/301.4R
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N	JP 08-283712	10-1996	Japan	----	----
	O	JP 2000-109826	04-2000	Japan	----	----
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-283712

(43)Date of publication of application : 29.10.1996

(51)Int.Cl.

C09K 11/64
H01J 61/44

(21)Application number : 07-090715

(71)Applicant : KASEI OPTONIX CO LTD
MITSUBISHI CHEM CORP

(22)Date of filing : 17.04.1995

(72)Inventor : HISAMUNE TAKAYUKI
NABE MASAKAZU
KAWA YUJI
KIJIMA NAOTO

(54) THREE-WAVELENGTH-REGION-EMISSION FLUORESCENT LAMP

(57)Abstract:

PURPOSE: To obtain a fluorescent lamp having high color rendering properties and a high efficiency and reduced in aging with time.

CONSTITUTION: The three-wavelength-region-emission fluorescent lamp having a fluorescent film made of a luminescent composition comprising a bivalent europium and manganese-coactivated alkaline earth metal aluminate phosphor represented by the formula: $\text{Ba}_{1-x-y}\text{Sr}_x\text{Eu}_y\text{Mg}_{1-z}\text{Mn}_z\text{Al}_{10}\text{O}_{17}$ (wherein x, y and z are in the ranges: $0.1 \leq x \leq 0.4$, $0.075 \leq y \leq 0.4$, and $0.005 \leq z \leq 0.05$).

LEGAL STATUS

[Date of request for examination] 18.06.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3475566

[Date of registration] 26.09.2003

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] General formula Three-wave region luminescence form fluorescent lamp characterized by having the fluorescent screen which the divalent europium and the manganese which are expressed with $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_z$ aluminum 10O17 (however, x, and y and z are numbers which fulfill $0.1 \leq x \leq 0.4$, $0.075 \leq y \leq 0.4$, and the conditions that become $0.005 \leq z \leq 0.05$, respectively) become from the luminescence constituent containing an activation alkaline earth aluminate fluorescent substance.

[Claim 2] Above x -- $0.1 \leq x \leq 0.15$ -- the time of being in the range -- Above y -- $0.2 \leq y \leq 0.4$ -- it is -- Above x -- $0.15 < x \leq 0.4$ -- the time of being in the range -- Above y -- $0.075 \leq y \leq 0.4$ -- the three-wave region luminescence form fluorescent lamp according to claim 1 characterized by being the number which fulfills conditions.

[Claim 3] Europium and manganese divalent [above-mentioned] are CuK α 1 to activation alkaline earth aluminate fluorescent substance powder. Three-wave region luminescence form fluorescent lamp according to claim 1 or 2 characterized by not having the diffraction peak of Miller indices 110, and the independent peak in the location of the diffraction peak of Miller indices 008 in the powder X diffraction pattern obtained when incidence of the characteristic X ray is carried out.

[Claim 4] A three-wave region luminescence form fluorescent lamp given in any 1 term of claim 1 characterized by containing a trivalent europium activation yttrium oxide fluorescent substance in the above-mentioned luminescence constituent thru/or claim 3.

[Claim 5] A three-wave region luminescence form fluorescent lamp given in any 1 term of claim 1 to which a terbium and a cerium are characterized by containing an activation phosphoric acid lanthanum fluorescent substance into the above-mentioned luminescence constituent thru/or claim 4.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the three-wave region luminescence form fluorescent lamp equipped with the alkaline earth aluminate fluorescent substance which ***** (ed) from divalent europium and divalent manganese as a fluorescent screen.

[0002]

[Description of the Prior Art] In recent years, in the field of the lamp for general lighting, a three-wave region luminescence form fluorescent lamp (on these specifications, a three-wave region luminescence form fluorescent lamp is only hereafter made to call it a "fluorescent lamp") is developed, and practical use is presented. The fluorescent substance used for this fluorescent lamp mixes the red and three sorts of green and blue fluorescent substances which have emission spectrum distribution of a narrow-band comparatively at a suitable rate. As for the fluorescent substance used for this fluorescent lamp, the oxidization yttrium of trivalent europium activation and the barium magnesium aluminate of the alkaline earth chloro phosphate or the divalent europium activation as a cerium and the phosphoric acid lanthanum of terbium activation, and a blue fluorescent substance as a green fluorescent substance are used as a red fluorescent substance, respectively.

[0003] This fluorescent lamp is excellent in the flux of light and both sides of color rendering properties, a general color rendering index (Ra) is 84, and the flux of light has realized 1470 lumens (lm) in floor line 20 SSEX-N/18 which are the fluorescent lamp of for example, a straight pipe mold. Furthermore, the fluorescent lamp which realized more than Ra=87 came to be used by adding a bluish green color or a bluish green color, and a deep red fluorescent substance to the three above-mentioned sorts of fluorescent substances, and mixing four sorts or five sorts of fluorescent substances. Furthermore, the fluorescent lamp beyond Ra=87 came to be realized by mixing of three sorts of fluorescent substances by specifying the presentation and the luminescent color of a divalent europium activation alkaline earth chloro phosphate fluorescent substance which are a blue component as made clear to JP, 5-302082, A.

[0004] On the other hand, about the fluorescent lamp which used the barium magnesium aluminate fluorescent substance of divalent europium activation as a blue component, what improved color rendering properties is put in practical use by ***** (ing) divalent manganese to the barium magnesium aluminate fluorescent substance of divalent europium activation. Moreover, it is indicated by using for JP, 56-86892, A the fluorescent substance expressed with $Ba_{1-x-y}Sr_xMg_pAl_qO_{1+p+q/2}Eu^{2+}$ (it is $0 < x \leq 0.1$, $0.01 \leq y \leq 0.4$, and $0.8 \leq p \leq 4.0$, $1.0 \leq q \leq 30$ here) that Ra=89 are realizable.

[0005] By the way, the fluorescent lamp which used the barium magnesium aluminate fluorescent substance of divalent europium activation as a blue component also has the problem that aging (color shift) of the luminescent color of the fluorescent lamp by degradation of a fluorescent substance is large, although the flux of light becomes high from the fluorescent lamp which used the divalent europium activation alkaline earth chloro phosphate fluorescent substance.

[0006] therefore, the mixing ratio with which the activation alkaline earth aluminate fluorescent substance was restricted for the europium activation oxidization yttrium (henceforth a "YOX red fluorescent substance"), the terbium, and the cerium to the europium activation alkaline earth aluminate fluorescent substance or the europium, and the manganese of a presentation which were restricted extremely with the activation phosphoric acid lanthanum (henceforth an "LAP green fluorescent substance") as an approach of solving this problem -- mixing and using it at a rate is indicated by JP, 4-106187, A and JP, 4-106188, A. However, implementation of a high color rendering and an efficient fluorescent lamp with few color shifts is desired further.

[0007]

[Problem(s) to be Solved by the Invention] Then, this invention aims at offering a high color rendering and an efficient three-wave region luminescence form fluorescent lamp with little degradation.

[0008]

[Means for Solving the Problem] The result of having examined many things about the fluorescent substance

presentations used and those combination in order to solve the above-mentioned purpose, While carrying out the specified quantity permutation of the one section of the barium of the barium magnesium aluminate fluorescent substance of divalent europium activation with strontium and carrying out the specified quantity permutation of the one section of magnesium with manganese The divalent europium and the manganese which set to 1:1:10 the ratio of the element of (Ba+Sr+Eu):(Mg+Mn):aluminum which constitutes a fluorescent substance an activation barium strontium magnesium aluminate fluorescent substance furthermore, with a YOX red fluorescent substance and an LAP green fluorescent substance By using the luminescence constituent which it comes to mix by the limited predetermined ratio as a fluorescent screen, it resulted that it was possible to offer a high color rendering and an efficient fluorescent lamp with little degradation in header this invention.

[0009] That is, the three-wave region luminescence form fluorescent lamp of this invention is general formula $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_z$ aluminum 10O17 (however, x, and y and z are numbers which fulfill $0.1 \leq x \leq 0.4$, $0.075 \leq y \leq 0.4$, and the conditions that become $0.005 \leq z \leq 0.05$, respectively.) the following -- being the same -- it is characterized by having the fluorescent screen which the divalent europium and the manganese which are expressed become from the luminescence constituent containing an activation alkaline earth aluminate fluorescent substance.

[0010]

[Function] Hereafter, the fluorescent lamp of this invention is explained to a detail. An activation alkaline earth aluminate fluorescent substance the divalent europium and the manganese which are used for the fluorescent lamp of this invention Ba, It mixes at a rate of satisfying empirical formula $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_z$ aluminum 10O17 for each oxide of Sr, Mg, aluminum, Eu, and Mn, or the compound of these elements which may change to these oxides easily at an elevated temperature at stoichiometric. It is obtained by calcinating [in a reducing atmosphere] once or more over 40 hours from 2 at 1200-1700 degrees C.

[0011] Thus, when, as for the reason degradation of this fluorescent substance with time be control although a degradation property with an activation barium strontium magnesium aluminate fluorescent substance with time be improve, the divalent europium and the manganese which be obtained permute the barium in a barium magnesium aluminate fluorescent substance parent in part with strontium, since the lattice constant c of fluorescent substance host crystal became short, consequently the location of the oxygen in a Ba-O layer be stable, it think.

[0012] Drawing 1 and drawing 2 the divalent europium and the manganese which are used as a blue luminescence fluorescent substance of the fluorescent lamp of this invention, respectively An activation barium strontium magnesium aluminate fluorescent substance ($Ba_{0.7}Sr_{0.2}Eu_{0.1}Mg_{0.98}Mn_{0.02}$ aluminum 10O17), The divalent europium and the manganese which are used as a blue luminescence fluorescent substance of the conventional fluorescent lamp and about an activation barium magnesium aluminate fluorescent substance ($Ba_{0.9}Eu_{0.1}Mg_{0.98}Mn_{0.02}$ aluminum 10O17) It is CuKalpha1 to this. The powder X diffraction pattern obtained when carrying out incidence of the characteristic X ray is illustrated. In the case of an activation barium strontium magnesium aluminate fluorescent substance (drawing 1), divalent europium and manganese do not have the maximal value independently in the location of Miller indices 008 with the diffraction peak of Miller indices 110. On the other hand, in the case of an activation barium magnesium aluminate fluorescent substance, divalent europium and manganese serve as a powder X diffraction pattern as shown in drawing 2, and it has the maximal value independently for them in the location of Miller indices 008 with the diffraction peak of Miller indices 110. Here, when it did not have the maximal value independently and 2theta is made into t times for X diffraction reinforcement whenever [1 and angle-of-diffraction], it means that primary differential value dl/dt does not have a negative value between the diffraction peak of Miller indices 008, and the diffraction peak of Miller indices 110.

[0013] The curves a and b of drawing 3 the divalent europium and the manganese which are used as a blue luminescence fluorescent substance of the fluorescent lamp of this invention, respectively Moreover, an activation barium strontium magnesium aluminate fluorescent substance, And it is what illustrates an emission spectrum when the divalent europium and the manganese which are used as a blue luminescence fluorescent substance of the conventional fluorescent lamp excite an activation barium magnesium aluminate fluorescent substance by 253.7nm ultraviolet rays. By permuting some barium of the conventional barium magnesium aluminate fluorescent substance with strontium so that the comparison of the curves a and b of drawing 3 may show (The curve a of drawing 3) the peak location of luminescence which originates in europium compared with the conventional barium magnesium aluminate fluorescent substance (the curve b of drawing 3) -- a long wave -- it moves to a merit side.

[0014] Furthermore, manganese is permuted by the location of magnesium in part, and is ***** (ed), and when this, a YOX red fluorescent substance, and an LAP green fluorescent substance are mixed by the predetermined quantitative ratio and it is used as a luminescence constituent of a fluorescent lamp, it becomes possible to offer a high color rendering and an efficient fluorescent lamp with little degradation. In addition, the divalent europium and the manganese which are the blue luminescence component of the luminescence constituent for fluorescent lamps of this invention are set to an activation barium strontium magnesium aluminate fluorescent substance ($Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_z$ aluminum 10O17). When x is in the range of $0.1 \leq x \leq 0.15$, y $0.2 \leq y \leq 0.4$ When the becoming conditions are

fulfilled and x is in the range of $0.15 < x \leq 0.4$, When the thing of a presentation which fulfills the conditions used as $0.075 \leq y \leq 0.4$ is used, there are few falls of the luminescence reinforcement of a fluorescent lamp with time, and a fluorescent lamp with little degradation with time is obtained.

[0015] In addition, when the depressor effect of the same degradation with time as the case where strontium permutes barium increases the addition of the europium which is an activator, it is obtained, and increasing the quantity of expensive europium also has the problem that not a best policy but degradation by baking at the time of fluorescent lamp manufacture if the addition of europium is increased again becomes large. Therefore, when comparing the property of the fluorescent lamp of this invention with the conventional fluorescent lamp, the lamps which used the blue fluorescent substance of the same europium concentration should compare.

[0016]

[Example]

(Example 1)

[0017]

[Table 1]

BaCO₃ 0.7 mol SrCO₃ 0.2 mol Eu₂O₃ 0.05 mol 3MgCO(s)₃ and Mg₂(OH) 0.245 mol MnO₂ 0.02 mol aluminum 2O₃ (gamma type) 5.0 mol AlF₃ 0.010 mol [0018] The above-mentioned raw material was mixed, crucible was filled up, the lump of a graphite was further picked up on the raw material, and it calcinated over 24 hours including rising-and-falling-temperature time amount at 1450 degrees C of maximum temperatures in the nitrogen hydrogen ambient atmosphere which covered and contained the steam.

[0019] Subsequently, distribution, washing, desiccation, and processing of a screen are performed for baking powder (the divalent europium of Ba_{0.7} Sr_{0.2} Eu_{0.1} OMg_{0.98}Mn_{0.02}aluminum 10O₁₇ and a manganese activation blue luminescence barium strontium magnesium aluminate fluorescent substance were obtained.). In addition, AlF₃ It is the flux often used for manufacture of a fluorescent substance. The emission spectrum of this fluorescent substance is shown in drawing 3 a. The luminescent color when exciting by the 253.7nm ultraviolet rays of this fluorescent substance was $x = 0.141$ and $y = 0.159$.

[0020] 28.0 % of the weight of fluorescent substances obtained as mentioned above, 35.2% of the weight of the YOX red fluorescent substance, and 36.8% of the weight of the LAP green fluorescent substance were fully mixed with the lacquer of a nitrocellulose to butyl acetate, the fluorescent substance slurry was produced, it applied to the glass tube, and the fluorescent lamp (FCL64T6) of color temperature 5000K was manufactured by the usual approach after desiccation.

[0021] Moreover, while mixing at a rate used as each empirical formula having shown the above-mentioned raw material in Table 1 and obtaining divalent europium and a manganese activation blue luminescence barium strontium magnesium aluminate fluorescent substance, the fluorescent lamp of examples 2-4 was obtained like the above-mentioned example 1 except using the luminescence constituent which mixed each color fluorescent substance of the rate shown in Table 1. Thus, the flux of light was 100 in the relative value which set the fluorescent lamp of the example 1 of the following comparison to 100, and the initial property of the obtained fluorescent lamp was average color-rendering-properties characteristic $R_a = 87.8$.

[0022] (Example 1 of a comparison) Apart from this, it is SrCO₃ [given in an example 1]. While mixing the raw material of an except at a rate used as the empirical formula of a publication for the example of a comparison of Table 1 and obtaining divalent europium and a manganese activation blue luminescence barium magnesium aluminate fluorescent substance, the fluorescent lamp of the example 1 of a comparison was obtained like the above-mentioned example 1 except using the luminescence constituent which mixed each color fluorescent substance of the rate shown in the example 1 of a comparison of Table 1. Thus, about the fluorescent lamp of the acquired examples 1-4 and the example 1 of a comparison, the result of having measured the luminescent chromaticity point (x , y value), the initial flux of light (relative value), and an average color rendering characteristic (R_a) is shown in Table 1 with the empirical formula of a blue luminescence fluorescent substance, and the mixing ratio of each fluorescent substance.

[0023]

[Table 2]

表 1

	青 色 萤 光 体				混合比 (重量%)			光 束 (相对值)	平均演色 評価数 (R a)
	組 成	発光色度点		青 色 萤光体	Y0X	LAP			
		x	y						
实施例 1	Ba _{0.7} Sr _{0.2} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	0.141	0.159	28.0	35.2	38.8	100	87.8	
实施例 2	Ba _{0.8} Sr _{0.3} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	0.142	0.169	28.6	35.7	35.7	100	88.8	
实施例 3	Ba _{0.8} Sr _{0.1} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	0.143	0.158	27.8	35.0	37.2	100	87.4	
实施例 4	Ba _{0.6} Sr _{0.3} Eu _{0.1} Mg _{0.988} Mn _{0.012} Al ₁₀ O ₁₇	0.142	0.188	26.4	34.1	39.5	101	87.8	
比較例 1	Ba _{0.9} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	0.143	0.155	27.9	34.7	37.4	100	86.9	

[0024] As for the fluorescent lamp (examples 1-5) of this invention, as compared with the fluorescent lamp of the example 1 of a comparison which used the blue fluorescent substance of the same europium concentration, the flux of light was the same, and an average color-rendering-properties characteristic's was improving, and color rendering properties have been improved more so that the result of a publication may show Table 1. Moreover, the degree of an improvement of degradation with the passage of time under fluorescent lamp lighting of the blue fluorescent substance which used the fluorescent lamp of examples 1-4 especially for the examples 1, 2, and 4 although it was checked that degradation with the passage of time is also improved was size a little compared with the thing of an example 3.

[0025] (An example 5, example 2 of a comparison) The blue fluorescent substance shown in Table 2 was used, and the three-wave region luminescence form fluorescent lamp of color temperature 5000K of FCL64T6 was produced by the same approach as an example 1. Thus, about the fluorescent lamp of the acquired example 5 and the example 2 of a comparison, the result of having measured the luminescent chromaticity point (x, y value), the initial flux of light (relative value), and an average color rendering characteristic (Ra) is shown in Table 1 with the empirical formula of a blue luminescence fluorescent substance, and the mixing ratio of each fluorescent substance.

[0026]

[Table 3]

表 2

	青 色 萤 光 体				混 合 比 (重 量 %)			光 束 (相对值)	平均演色 評価数 (R a)
	組 成	発光色度点		青 色 萤光体	Y0X	LAP			
		x	y						
実施例 5	Ba _{0.7} Sr _{0.1} Eu _{0.2} Mg _{0.988} Mn _{0.014} Al ₁₀ O ₁₇	0.142	0.169	28.0	35.9	36.1	100	89.1	
比較例 2	Ba _{0.8} Eu _{0.2} Mg _{0.988} Mn _{0.014} Al ₁₀ O ₁₇	0.143	0.167	28.1	35.6	36.3	100	88.7	

[0027] As compared with the fluorescent lamp of the example 2 of a comparison which used the blue fluorescent substance of the europium concentration with the same fluorescent lamp of this invention of an example 5, the flux of light was the same, and its average color-rendering-properties characteristic was improving, and color rendering properties have been improved more so that the result of a publication may show Table 2. In addition, compared with the fluorescent lamp of the example 2 of a comparison, as for the fluorescent lamp of an example 5, it was checked that degradation with the passage of time is also improved. Moreover, the example 3 was excelled in the field of degradation with the passage of time a little.

[0028] (An example 6, example 3 of a comparison) The blue fluorescent substance shown in Table 3 was used, and the three-wave region luminescence form fluorescent lamp of color temperature 5000K of FCL64T6 was produced by the same approach as an example 1. Thus, about the fluorescent lamp of the acquired example 6 and the example 3 of a comparison, the result of having measured the luminescent chromaticity point (x, y value), the initial flux of light (relative value), and an average color rendering characteristic (Ra) is shown in Table 1 with the empirical formula of a blue luminescence fluorescent substance, and the mixing ratio of each fluorescent substance.

[0029]

[Table 4]

表 2

	青 色 螢 光 体				混 合 比 (重量%)			光 束 (相 对 值)	平均演色 評価数 (R a)
	組 成	発光色度点		青 色 螢光体	YOX	LAP			
		x	y						
実施例 6	Ba _{0.65} Sr _{0.2} Eu _{0.15} Mg _{0.08} Mn _{0.02} Al ₁₀ O ₁₇	0.142	0.186	29.1	36.8	34.1	100	89.2	
比較例 3	Ba _{0.65} Eu _{0.15} Mg _{0.08} Mn _{0.02} Al ₁₀ O ₁₇	0.142	0.173	28.2	36.1	34.1	100	88.1	

[0030] As compared with the fluorescent lamp of the example 3 of a comparison which used the blue fluorescent substance of the europium concentration with the same fluorescent lamp of this invention of an example 6, the flux of light was the same, and its average color-rendering-properties characteristic was improving, and color rendering properties have been improved more so that the result of a publication may show Table 3. In addition, compared with the fluorescent lamp of the example 3 of a comparison, as for the fluorescent lamp of an example 6, it was checked that degradation with the passage of time is also improved. Moreover, it excelled a little in respect of [example / 3] degradation with the passage of time.

[0031]

[Effect of the Invention] According to this invention, a high color rendering and a fluorescent lamp with little degradation with the passage of time can be offered efficient.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平8-283712

(43) 公開日 平成8年(1996)10月29日

(51) Int.Cl. ⁶	識別記号	庁内整理番号	F I	技術表示箇所
C 0 9 K 11/64	CPM	9280-4H	C 0 9 K 11/64	CPM
H 0 1 J 61/44			H 0 1 J 61/44	N

審査請求 未請求 請求項の数5 O L (全 7 頁)

(21) 出願番号 特願平7-90715

(22) 出願日 平成7年(1995)4月17日

(71) 出願人 390019976

化成オプトニクス株式会社

東京都港区芝公園一丁目8番12号

(71) 出願人 000005968

三菱化学株式会社

東京都千代田区丸の内二丁目5番2号

(72) 発明者 久宗 孝之

神奈川県小田原市成田1060番地 化成オプトニクス株式会社小田原工場内

(72) 発明者 那部 正和

神奈川県小田原市成田1060番地 化成オプトニクス株式会社小田原工場内

(74) 代理人 弁理士 長谷川 曉司

最終頁に続く

(54) 【発明の名称】 3波長域発光形蛍光ランプ

(57) 【要約】

【構成】 一般式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$

(但し、 x 、 y 及び z はそれぞれ $0.1 \leq x \leq 0.4$ 、 $0.075 \leq y \leq 0.4$ 及び $0.005 \leq z \leq 0.05$ なる条件を満たす数である)で表される、2価のユーロビウム及びマンガン共付活アルカリ土類アルミン酸塩蛍光体を含む発光組成物からなる蛍光膜を有することを特徴とする3波長域発光形蛍光ランプ。

【効果】 本発明によれば、高演色、高効率で、かつ経時劣化の少ない蛍光ランプを提供することが出来る。

【特許請求の範囲】

【請求項1】 一般式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ (但し、 x 、 y 及び z はそれぞれ $0.1 \leq x \leq 0.4$ 、 $0.075 \leq y \leq 0.4$ 及び $0.005 \leq z \leq 0.05$ なる条件を満たす数である)で表される、2価のユーロビウム及びマンガン共付活アルカリ土類アルミン酸塩蛍光体を含む発光組成物からなる蛍光膜を有することを特徴とする3波長域発光形蛍光ランプ。

【請求項2】 上記 x が $0.1 \leq x \leq 0.15$ なる範囲にあるとき、上記 y が $0.2 \leq y \leq 0.4$ であり、上記 x が $0.15 < x \leq 0.4$ なる範囲にあるとき、上記 y が $0.075 \leq y \leq 0.4$ なる条件を満たす数であることを特徴とする請求項1記載の3波長域発光形蛍光ランプ。

【請求項3】 上記2価のユーロビウム及びマンガン共付活アルカリ土類アルミン酸塩蛍光体粉末に $CuK\alpha_1$ 特性X線を入射した際に得られる粉末X線回折パターンにおける、ミラー指数008の回折ピークの位置にミラー指数110の回折ピークと独立したピークを有さないことを特徴とする請求項1又は請求項2記載の3波長域発光形蛍光ランプ。

【請求項4】 上記発光組成物中に3価のユーロビウム付活酸化イットリウム蛍光体が含まれることを特徴とする請求項1乃至請求項3のいずれか1項に記載の3波長域発光形蛍光ランプ。

【請求項5】 上記発光組成物中にテルビウム及びセリウム共付活燐酸ランタン蛍光体が含まれることを特徴とする請求項1乃至請求項4のいずれか1項に記載の3波長域発光形蛍光ランプ。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は2価のユーロビウム及び2価のマンガンで共付活したアルカリ土類アルミン酸塩蛍光体を蛍光膜として備えた3波長域発光形蛍光ランプに関する。

【0002】

【従来の技術】近年、一般照明用ランプの分野で、3波長域発光形蛍光ランプ(以下、本明細書では3波長域発光形蛍光ランプを単に、「蛍光ランプ」と言うことにする)が開発され、実用に供されている。この蛍光ランプに使用される蛍光体は、比較的狭帯域の発光スペクトル分布を有する赤色、緑色、青色の3種の蛍光体を適当な割合で混合したものである。この蛍光ランプに使用される蛍光体は、赤色蛍光体として3価のユーロビウム付活の酸化イットリウム、緑色蛍光体としてセリウム及びテルビウム付活の燐酸ランタン、青色蛍光体としてアルカリ土類クロロ燐酸塩あるいは、2価のユーロビウム付活のバリウムマグネシウムアルミン酸塩がそれぞれ使用されている。

【0003】この蛍光ランプは、光束、演色性の両面で優れており、平均演色評価数(Ra)が84で、光束は例えば、直管型の蛍光ランプである、FL20SSEX-N/18では1470ルーメン(1m)を実現している。更に上記3種の蛍光体に、青緑色、あるいは青緑色と深赤色蛍光体を加え、4種あるいは5種の蛍光体を混合することにより、Ra=87以上を実現した蛍光ランプが実用されるようになった。更には特開平5-302082号公報に明らかにされているように、青色成分である2価のユーロビウム付活アルカリ土類クロロ燐酸塩蛍光体の組成及び発光色を特定することにより、3種のみの蛍光体の混合によりRa=87以上の蛍光ランプが実現されるようになった。

【0004】一方、青色成分として2価のユーロビウム付活のバリウムマグネシウムアルミン酸塩蛍光体を使用した蛍光ランプに関しては、2価のユーロビウム付活のバリウムマグネシウムアルミン酸塩蛍光体に2価のマンガン共付活することによって演色性を向上したものが実用化されている。また、特開昭56-86892号公報には、 $Ba_{1-x-y}Sr_xMg_pAl_qO_{1+p+q/2}Eu^{2+}$ (ここで $0 < x \leq 0.1$ 、 $0.01 \leq y \leq 0.4$ 、 $0.8 \leq p \leq 4.0$ 、 $1.0 \leq q \leq 3.0$)で表される蛍光体を用いることにより、Ra=89を実現できることが開示されている。

【0005】ところで、青色成分として2価のユーロビウム付活のバリウムマグネシウムアルミン酸塩蛍光体を使用した蛍光ランプは、2価のユーロビウム付活アルカリ土類クロロ燐酸塩蛍光体を用いた蛍光ランプより光束が高くなるが、蛍光体の劣化による蛍光ランプの発光色の経時変化(カラーシフト)が大きいという問題もある。

【0006】そのためこの問題を解決する方法として、極めて限られた組成のユーロビウム付活アルカリ土類アルミン酸塩蛍光体あるいはユーロビウム及びマンガン共付活アルカリ土類アルミン酸塩蛍光体をユーロビウム付活酸化イットリウム(以下、「YOX赤色蛍光体」という)及びテルビウム及びセリウム共付活燐酸ランタン(以下、「LAP緑色蛍光体」という)と共に限られた混合比率で混合して使用することが、特開平4-106187号公報や特開平4-106188号公報に開示されている。しかしながら、より一層高演色、高効率でかつカラーシフトの少ない蛍光ランプの実現が望まれている。

【0007】

【発明が解決しようとする課題】そこで本発明は、高演色、高効率でかつ劣化の少ない3波長域発光形蛍光ランプを提供することを目的とする。

【0008】

【課題を解決するための手段】上記目的を解決するため、用いられる蛍光体組成およびそれらの組み合わせに

について種々検討した結果、2価のユーロピウム付活のバリウムマグネシウムアルミン酸塩蛍光体のバリウムの1部をストロンチウムによって所定量置換し、かつ、マグネシウムの1部をマンガンによって所定量置換すると共に、更に蛍光体を構成する(Ba+Sr+Eu):(Mg+Mn):Alの元素の比を1:1:10とした2価のユーロピウム及びマンガン共付活バリウムストロンチウムマグネシウムアルミン酸塩蛍光体をYOX赤色蛍光体及びLAP緑色蛍光体と共に限られた所定の比率で混合してなる発光組成物を蛍光膜として使用することにより、高演色、高効率でかつ劣化の少ない蛍光ランプを提供することが可能であることを見出し本発明に至った。

【0009】即ち本発明の3波長域発光形蛍光ランプは、一般式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ (但し、x、y及びzはそれぞれ $0.1 \leq x \leq 0.4$ 、 $0.075 \leq y \leq 0.4$ 及び $0.005 \leq z \leq 0.05$ なる条件を満たす数である。以下、同様である) で表される、2価のユーロピウム及びマンガン共付活アルカリ土類アルミン酸塩蛍光体を含む発光組成物からなる蛍光膜を有することを特徴とする。

【0010】

【作用】以下、本発明の蛍光ランプについて詳細に説明する。本発明の蛍光ランプに使用される2価のユーロピウム及びマンガン共付活アルカリ土類アルミン酸塩蛍光体はBa、Sr、Mg、Al、Eu及びMnの各酸化物又は高温で容易にこれらの酸化物に変わり得るこれらの元素の化合物を化学量論的に組成式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ を満足する割合で混合し、還元性雰囲気中で1200~1700℃で2から40時間かけて1回以上焼成することによって得られる。

【0011】このようにして得られた2価のユーロピウム及びマンガン共付活バリウムストロンチウムマグネシウムアルミン酸塩蛍光体は経時的な劣化特性が改善されるが、この蛍光体の経時的な劣化が抑制される理由は、バリウムマグネシウムアルミン酸塩蛍光体母体中のバリウムをストロンチウムで一部置換することにより、蛍光体母体結晶の格子定数cが短くなり、その結果、Ba-O層内の酸素の位置が安定化したためと考えられる。

【0012】図1及び図2はそれぞれ、本発明の蛍光ランプの青色発光蛍光体として使用される2価のユーロピウム及びマンガン共付活バリウムストロンチウムマグネシウムアルミン酸塩蛍光体 ($Ba_{0.7}Sr_{0.2}Eu_{0.1}Mg_{0.98}Mn_{0.02}Al_{10}O_{17}$)、及び従来の蛍光ランプの青色発光蛍光体として使用される2価のユーロピウム及びマンガン共付活バリウムマグネシウムアルミン酸塩蛍光体 ($Ba_{0.9}Eu_{0.1}Mg_{0.98}Mn_{0.02}Al_{10}O_{17}$) について、これにCuK α_1 の特性X線を入射させた際に得られる粉末X線回折パターンを例示したものであり、2価のユーロピウム及びマンガン共付活バリウムストロンチウムマグネシウムアルミン酸塩蛍光体

(図1)の場合、ミラー指数008の位置にミラー指数110の回折ピークと独立して極大値を持たない。一方、2価のユーロピウム及びマンガン共付活バリウムマグネシウムアルミン酸塩蛍光体の場合は図2に示すような粉末X線回折パターンとなり、ミラー指数008の位置にミラー指数110の回折ピークと独立して極大値を持つ。ここで、独立して極大値を持たないとは、X線回折強度を1、回折角度2 θ をも度とした場合に、一次微分値d1/d θ がミラー指数008の回折ピークとミラー指数110の回折ピークの間において、負の値を持たないことを意味する。

【0013】また、図3の曲線a及びbはそれぞれ、本発明の蛍光ランプの青色発光蛍光体として使用される2価のユーロピウム及びマンガン共付活バリウムストロンチウムマグネシウムアルミン酸塩蛍光体、及び従来の蛍光ランプの青色発光蛍光体として使用される2価のユーロピウム及びマンガン共付活バリウムマグネシウムアルミン酸塩蛍光体を253.7nmの紫外線で励起した時の発光スペクトルを例示するものであり、図3の曲線a及びbの比較からわかるように、従来のバリウムマグネシウムアルミン酸塩蛍光体のバリウムの一部をストロンチウムで置換することによって(図3の曲線a)、従来のバリウムマグネシウムアルミン酸塩蛍光体(図3の曲線b)に比べてユーロピウムに起因する発光のピーク位置が、長波長側に移動する。

【0014】更にマンガンをマグネシウムの位置に一部置換して共付活し、これとYOX赤色蛍光体とLAP緑色蛍光体とを所定の量比で混合して蛍光ランプの発光組成物として使用した場合、高演色、高効率で、かつ劣化の少ない蛍光ランプを提供することが可能となる。なお、本発明の蛍光ランプ用発光組成物の青色発光成分である2価のユーロピウム及びマンガン共付活バリウムストロンチウムマグネシウムアルミン酸塩蛍光体 ($Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$) において、xが $0.1 \leq x \leq 0.15$ の範囲にある場合はyが $0.2 \leq y \leq 0.4$ なる条件を満たし、xが $0.15 < x \leq 0.4$ の範囲にあるとき、 $0.075 \leq y \leq 0.4$ となる条件を満たす組成のものをを用いた場合、蛍光ランプの経時的な発光強度の低下が少なく、経時的劣化の少ない蛍光ランプが得られる。

【0015】なお、バリウムをストロンチウムで置換した場合と同様の経時的劣化の抑制効果は、付活剤であるユーロピウムの添加量を増すことによっても得られるが、高価なユーロピウムを増量することは得策でなく、また、ユーロピウムの添加量を増すと蛍光ランプ製造時のベークキングによる劣化が大きくなるという問題もある。従って、本発明の蛍光ランプの特性を従来の蛍光ランプと比較する場合には、同じユーロピウム濃度の青色蛍光体を使用したランプ同士で比較すべきである。

【0016】

【実施例】

(実施例1)

*【0017】

*【表1】

BaCO ₃	0.7	mol
SrCO ₃	0.2	mol
Eu ₂ O ₃	0.05	mol
3MgCO ₃ · Mg(OH) ₂	0.245	mol
MnO ₂	0.02	mol
Al ₂ O ₃ (ガンマタイプ)	5.0	mol
AlF ₃	0.010	mol

【0018】上記原料を混合し、坩堝に充填し、更に黒鉛の塊を原料の上に乗せ、蓋をして水蒸気を含んだ窒素水素雰囲気中で最高温度1450℃で昇降温時間を含めて24時間掛けて焼成した。

【0019】次いで、焼成粉を分散、洗浄、乾燥、篩の処理を行い(Ba_{0.7}Sr_{0.2}Eu_{0.1}OMg_{0.98}Mn_{0.02}Al₁₀O₁₇の2価のユーロピウム及びマンガン付活青色発光バリウムストロンチウムマグネシウムアルミン酸塩蛍光体を得た。なお、AlF₃は蛍光体の製造にしばしば用いられるフラックスである。この蛍光体の発光スペクトルを図3aに示す。この蛍光体の253.7nmの紫外線で励起したときの発光色はx=0.141、y=0.159であった。

【0020】上述のようにして得られた蛍光体28.0重量%と、35.2重量%のYOX赤色蛍光体と、36.8重量%のLAP緑色蛍光体とを酢酸ブチルにニトロセルロースのラッカーと共に充分に混合して蛍光体スラリーを作製し、ガラス管に塗布して乾燥後、通常の方法で色温度5000Kの蛍光ランプ(FCL64T6)を製造した。

【0021】また、上記原料を表1に示した各組成式となる割合で混合して2価のユーロピウム及びマンガン付※

10※活青色発光バリウムストロンチウムマグネシウムアルミン酸塩蛍光体を得ると共に、表1に示した割合の各色蛍光体を混合した発光組成物を用いる以外は上記実施例1と同様にして実施例2～4の蛍光ランプを得た。このようにして得られた蛍光ランプの初期特性は、光束が下記比較例1の蛍光ランプを100とした相対値で100であり、平均演色性指数Ra=87.8であった。

【0022】(比較例1)これとは別に実施例1に記載のSrCO₃以外の原料を表1の比較例に記載の組成式となる割合で混合して2価のユーロピウム及びマンガン付活青色発光バリウムマグネシウムアルミン酸塩蛍光体を得ると共に、表1の比較例1に示した割合の各色蛍光体を混合した発光組成物を用いる以外は上記実施例1と同様にして比較例1の蛍光ランプを得た。このようにして得られた実施例1～4及び比較例1の蛍光ランプについて、その発光色度点(x、y値)、初期光束(相対値)及び平均演色指数(Ra)を測定した結果を青色発光蛍光体の組成式、各蛍光体の混合比と共に表1に示す。

【0023】

【表2】

表 1

	青 色 蛍 光 体				混合比 (重量%)			光 束 (相対値)	平均演色 評価数 (R a)
	組 成	発光色度点		青 色 蛍 光 体	YOX	LAP			
		x	y						
実施例 1	Ba _{0.7} Sr _{0.2} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	0.141	0.159	28.0	35.2	36.8	100	87.8	
実施例 2	Ba _{0.8} Sr _{0.3} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	0.142	0.169	28.6	35.7	35.7	100	88.8	
実施例 3	Ba _{0.8} Sr _{0.1} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	0.143	0.158	27.8	35.0	37.2	100	87.4	
実施例 4	Ba _{0.8} Sr _{0.3} Eu _{0.1} Mg _{0.988} Mn _{0.012} Al ₁₀ O ₁₇	0.142	0.136	26.4	34.1	39.5	101	87.8	
比較例 1	Ba _{0.9} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	0.143	0.155	27.9	34.7	37.4	100	86.9	

【0024】表1に記載の結果からわかるように、本発明の蛍光ランプ(実施例1～5)は、同じユーロピウム濃度の青色蛍光体を使用した、比較例1の蛍光ランプと比較して、光束は同じでかつ平均演色性指数が向上しており、演色性がより改善された。また、実施例1～4の蛍光ランプは経時劣化も改善されていることが確認されたが、特に実施例1、2及び4に使用した青色蛍光体の★50

★蛍光ランプ点灯中の経時劣化の改善の度合いは実施例3のものに比べ若干大であった。

【0025】(実施例5、比較例2)表2に示す青色蛍光体を使用し、実施例1と同様の方法でFCL64T6の色温度5000Kの3波長域発光形蛍光ランプを作製した。このようにして得られた実施例5及び比較例2の蛍光ランプについて、その発光色度点(x、y値)、初

期光束（相対値）及び平均演色指数（Ra）を測定した *【0026】
結果を青色発光蛍光体の組成式、各蛍光体の混合比と共に 【表3】
に表1に示す。

*
表 2

	青 色 蛍 光 体						混合比 (重量%)			光 束 (相対値)	平均演色 評価数 (Ra)		
	組 成						青 色 蛍 光 体	YOX	LAP				
												x	y
実施例 5	Ba _{0.7} Sr _{0.1} Eu _{0.2} Mg _{0.988} Mn _{0.014} Al ₁₀ O ₁₇						0.142	0.169	28.0	35.9	36.1	100	88.1
比較例 2	Ba _{0.8} Eu _{0.2} Mg _{0.988} Mn _{0.014} Al ₁₀ O ₁₇						0.143	0.167	28.1	35.6	36.3	100	88.7

【0027】表2に記載の結果からわかるように、実施例5の本発明の蛍光ランプは、同じユーロピウム濃度の青色蛍光体を使用した、比較例2の蛍光ランプと比較して、光束は同じでかつ平均演色指数が向上しており、演色性がより改善された。尚、実施例5の蛍光ランプは比較例2の蛍光ランプに比べて経時劣化も改善されていることが確認された。また、経時劣化の面で実施例3より若干優れていた。

※光体を使用し、実施例1と同様の方法でFCL64T6の色温度5000Kの3波長域発光形蛍光ランプを作製した。このようにして得られた実施例6及び比較例3の蛍光ランプについて、その発光色度点（x、y値）、初期光束（相対値）及び平均演色指数（Ra）を測定した結果を青色発光蛍光体の組成式、各蛍光体の混合比と共に表1に示す。

20 【0029】

【0028】（実施例6、比較例3）表3に示す青色蛍※

表 2

	青 色 蛍 光 体					混合比 (重量%)			光 束 (相対値)	平均演色 評価数 (Ra)
	組 成		発光色度点		青 色 蛍光体	YOX	LAP			
			x	y						
実施例 6	Ba _{0.65} Sr _{0.2} Eu _{0.15} Mg _{0.08} Mn _{0.02} Al ₁₀ O ₁₇		0.142	0.166	29.1	36.8	34.1	100	89.2	
比較例 3	Ba _{0.65} Eu _{0.15} Mg _{0.08} Mn _{0.02} Al ₁₀ O ₁₇		0.142	0.173	28.2	36.1	34.1	100	88.1	

【0030】表3に記載の結果からわかるように、実施例6の本発明の蛍光ランプは、同じユーロピウム濃度の青色蛍光体を使用した、比較例3の蛍光ランプと比較して、光束は同じでかつ平均演色指数が向上しており、演色性がより改善された。尚、実施例6の蛍光ランプは比較例3の蛍光ランプに比べて経時劣化も改善されていることが確認された。また、経時劣化の面で実施例3より若干優れていた。

【0031】

【発明の効果】本発明によれば、高演色、高効率で、かつ経時劣化の少ない蛍光ランプを提供することが出来る。

【図面の簡単な説明】

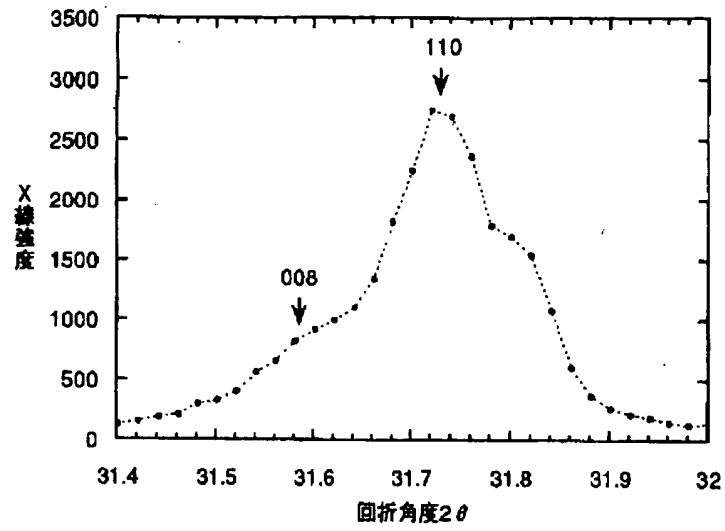
【図1】本発明の蛍光ランプに使用する2価のユーロピ★

★ウム及びマンガン付活青色発光バリウムストロンチウムマグネシウムアルミン酸塩蛍光体の粉末X線回折パターンを例示する図である。

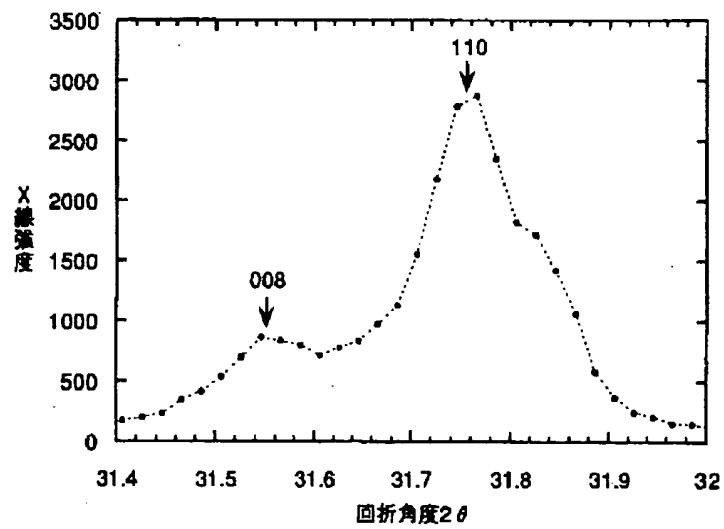
【図2】従来の蛍光ランプに使用する2価のユーロピウム及びマンガン付活青色発光バリウムマグネシウムアルミン酸塩蛍光体の粉末X線回折パターンを例示する図である。

【図3】本発明の蛍光ランプに使用する2価のユーロピウム及びマンガン付活青色発光バリウムストロンチウムマグネシウムアルミン酸塩蛍光体及び従来の蛍光ランプに使用する2価のユーロピウム及びマンガン付活青色発光バリウムマグネシウムアルミン酸塩蛍光体を253.7nmの紫外線で励起したときの発光スペクトルを例示する図である。

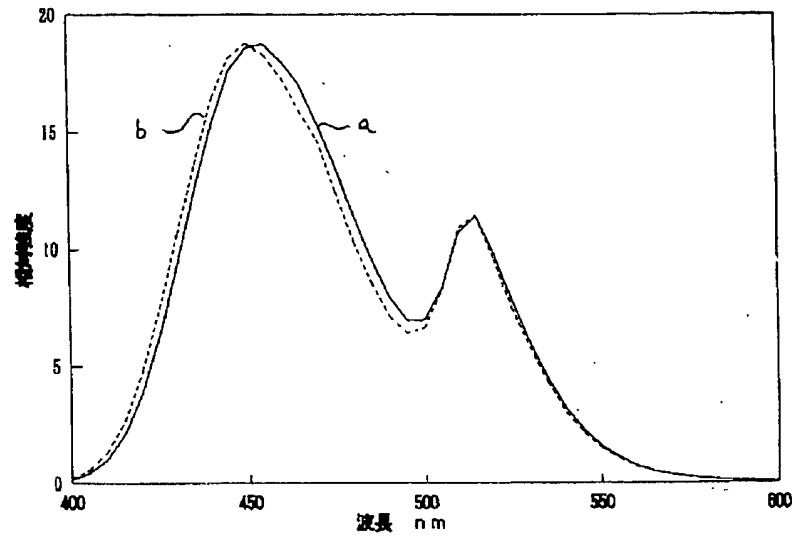
【図1】



【図2】



【図3】



フロントページの続き

(72)発明者 川 裕司
神奈川県小田原市成田1060番地 化成オブ
トニクス株式会社小田原工場内

(72)発明者 木島 直人
神奈川県横浜市青葉区鴨志田町1000番地
三菱化学株式会社横浜総合研究所内

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-109826

(43)Date of publication of application : 18.04.2000

(51)Int.Cl.

C09K 11/64

C09K 11/80

H01J 61/44

(21)Application number : 10-282311

(71)Applicant : KASEI OPTONIX CO LTD

(22)Date of filing : 05.10.1998

(72)Inventor : OTSUKA REIJI
ISHII HIROFUMI

(54) FLUORESCENT SUBSTANCE OF ALKALINE EARTH ALUMINATE AND FLUORESCENT LAMP

(57)Abstract:

PROBLEM TO BE SOLVED: To control lapsing deterioration on changes of luminous color and on luminous efficiency during lighting a fluorescent lamp as well as to improve coloring action and the efficiency by comprising a specific composition of Ba, Sr, Eu, Mg, Mn, Al and O.

SOLUTION: A fluorescent substance is represented by a compositional formula, $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_2Al_{10}O_{17}$. In the formula, (x), (y) and (z), fulfill $0.4 \leq x \leq 0.6$, $0.03 \leq y \leq 0.3$, $0 \leq z \leq 0.04$, respectively. This fluorescent substance is obtained by mixing each oxide of Ba, Sr, Mg, Al, Eu and Mn or mixing compounds generating readily these oxides at a high temperature so as to make a stoichiometric ratio of this compositional formula, and this mixture is charged into a heat-resistant container followed by one or more of calcining at 1200-1700°C for 2-40 hr in a reductive atmosphere. When this fluorescent substance is used as a blue luminous component of the luminous composition of a fluorescent lamp, the lamp which is less in lapsing deterioration with high coloring action and high efficiency, can be obtained.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of
rejection]

[Date of requesting appeal against examiner's

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] General formula Alkaline earth aluminate fluorescent substance characterized by what it is expressed with $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_z$ aluminum 10O17, and is expressed with the number with which x in a formula, and y and z fill $0.4 \leq x \leq 0.6$, $0.03 \leq y \leq 0.3$, and the conditions that become $0 \leq z \leq 0.04$, respectively.

[Claim 2] The fluorescent lamp characterized by coming to form the fluorescent substance layer of a glass tube wall using an alkaline earth aluminate fluorescent substance according to claim 1.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] General formula Alkaline earth aluminate fluorescent substance characterized by what it is expressed with $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_z$ aluminum 10O17, and is expressed with the number with which x in a formula, and y and z fill $0.4 \leq x \leq 0.6$, $0.03 \leq y \leq 0.3$, and the conditions that become $0 \leq z \leq 0.04$, respectively.

[Claim 2] The fluorescent lamp characterized by coming to form the fluorescent substance layer of a glass tube wall using an alkaline earth aluminate fluorescent substance according to claim 1.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the alkaline earth aluminate fluorescent substance which activated with divalent europium (Eu²⁺), or *****(ed) from divalent europium (Eu²⁺) and divalent manganese (Mn²⁺), and the three-wave region luminescence mold fluorescent lamp using this fluorescent substance as a fluorescent screen of a blue luminescence component.

[0002]

[Description of the Prior Art] In recent years, in the field of the fluorescent lamp for general lighting, a three-wave region luminescence mold fluorescent lamp (only henceforth a "fluorescent lamp") is developed, and practical use is presented. The fluorescent substance used for this fluorescent lamp mixes the red and three sorts of green and blue fluorescent substances which have emission spectrum distribution of a narrow-band comparatively at a suitable rate.

[0003] As for the fluorescent substance used for this fluorescent lamp, alkaline earth chloro phosphate or the barium magnesium aluminate of divalent europium (Eu²⁺) activation is used [as the oxidation yttrium of trivalent europium (Eu³⁺) activation, and a green fluorescent substance] as a red fluorescent substance, respectively as a cerium (Ce) and the phosphoric acid lanthanum of terbium (Tb) activation, and a blue fluorescent substance.

[0004] This fluorescent lamp is excellent in the flux of light and both sides of color rendering properties, a general color rendering index (Ra) is 84, and the flux of light has realized 1470 lumens (lm) in floor line 20 SSEX-N/18 of for example, a straight pipe mold fluorescent lamp. Furthermore, the fluorescent lamp which realized general-color-rendering-index Ra \geq 87 came to be used by adding the fluorescent substance of a bluish green color or a bluish green color, and deep red to the three above-mentioned sorts of fluorescent substances, and mixing four sorts or five sorts of fluorescent substances. Moreover, in JP, 5-302082, A, the fluorescent lamp of general-color-rendering-index Ra \geq 87 came to be realized by mixing of three sorts of fluorescent substances by specifying the presentation and the luminescent color of an Eu²⁺ activation alkaline earth chloro phosphate fluorescent substance which are a blue component.

[0005] On the other hand, about the fluorescent lamp which used the Eu²⁺ activation barium magnesium aluminate fluorescent substance as a blue component, what raised color rendering properties is put in practical use by *****(ing) Mn²⁺ to an Eu²⁺ activation barium magnesium aluminate fluorescent substance. Moreover, it is indicated by using for JP, 56-86892, A the fluorescent substance expressed with Ba_{1-x-y} Sr_x Mg_p Al_q O_{(1+p+q)/2} · Eu_{2+y} (here, it is 0 < x \leq 0.1, 0.01 \leq y \leq 0.4, 0.8 \leq p \leq 4.0, and 10 \leq q \leq 30) that general-color-rendering-index Ra=89 are realizable.

[0006] By the way, the fluorescent lamp which used the barium magnesium aluminate fluorescent substance of Eu²⁺ activation as a blue component also had the problem that aging (color shift) of the luminescent color of the fluorescent lamp by degradation of a fluorescent substance was large, although the flux of light became high from the fluorescent lamp which used the Eu²⁺ activation alkaline earth chloro phosphate fluorescent substance. The alkaline earth aluminate fluorescent substance activated as an approach of solving this problem by Eu²⁺, or Eu²⁺ and Mn²⁺ of the presentation restricted extremely Eu³⁺ activation yttrium oxide the mixing ratio to which (it being hereafter called a "YOX red fluorescent substance") and the phosphoric acid lanthanum (henceforth an "LAP green fluorescent substance") which *****(ed) by Tb and Ce were restricted -- mixing and using it at a rate is proposed by JP, 4-106187, A or JP, 4-106188, A.

[0007] furthermore, to JP, 3-106988, A (Ba_{1-x-y} Sr_x My) O_a (Mg_{1-p-q} Mn_p Zn_q) O_b Al₂ O₃ (M expresses at least one sort of elements of Sr and the calcium here) a, b, x, y, p, and q in a formula a³ \leq b \leq 4a^{3/2}, a^{7/3} - 1 \leq b \leq (11/9)a^{17/3}, Using the fluorescent substance expressed with 0 < x \leq 0.4, 0 \leq y \leq 0.4, 0 < x+y \leq 0.4, 0.001 < (ap/x) \leq 0.2, 0 \leq q \leq 0.3, and 0 \leq p+q \leq 0.3 for the same purpose as the above is proposed.

[0008] However, implementation of a high color rendering and a fluorescent lamp with few [it is efficient and] color shifts by degradation of the luminescent color with the passage of time is further desired rather than the fluorescent lamp using these aluminate fluorescent substances and phosphate fluorescent substances. Although the luminous

efficiency of the aluminate fluorescent substance used from the former as a blue luminescence fluorescent substance for high color-rendering-properties fluorescent lamps is also high, and it can make with the comparatively good fluorescent lamp of a general color rendering index (Ra) when this is used for a fluorescent lamp. When this is used for a fluorescent lamp by increasing the addition of Mn in the case of the aluminate fluorescent substance which contains Mn as an activator especially, it becomes [effectiveness (flux of light when emitting the white light)] low in that case and is not desirable to raise the general color rendering index (Ra) of a lamp, although it is possible. So, even if it is in an aluminate fluorescent substance, when this is used as a blue luminescence fluorescent substance for high color-rendering-properties fluorescent lamps, development of the aluminate fluorescent substance with which the general color rendering index (Ra) and luminous efficiency of a lamp can serve as a both more high fluorescent substance is desired.

[0009]

[Problem(s) to be Solved by the Invention] Then, in the alkaline earth aluminate fluorescent substance of the conventional Eu^{2+} activation or activation of Eu^{2+} and Mn^{2+} , this invention cancels the above-mentioned fault, provides a high color rendering, the efficient and small fluorescent substance of change of the luminescent color under fluorescent lamp lighting, and degradation of luminous efficiency with the passage of time, and a list with a fluorescent lamp, and presupposes like.

[0010]

[Means for Solving the Problem] The result which this invention person etc. examined in the detail further about the presentation of the alkaline earth fluorescent substance used for a fluorescent lamp for solution of the above-mentioned technical problem, When the fluorescent substance of more presentation fields than the alkaline earth aluminate fluorescent substance with which the content of the strontium in the parent of an alkaline earth aluminate fluorescent substance (Sr) is used from the former is used as a blue luminescence fluorescent substance for high color-rendering-properties fluorescent lamps, Even when not ***** (ing) Mn even if it lessened the amount of activation of Mn of this fluorescent substance and, it turned out that higher Ra value and luminous efficiency are shown. Namely, the specified quantity permutation of the one section of the barium (Ba) of the alkaline earth aluminate fluorescent substance of the Eu^{2+} activation containing barium (Ba) and magnesium (Mg) is carried out with strontium (Sr). Furthermore, the specified quantity permutation of the one section of magnesium (Mg) is carried out with manganese (Mn) if needed. The component (Ba+Sr+Eu):(Mg+Mn) component which constitutes a fluorescent substance : The ratio of each element of aluminum component is set to 1:1:10. About the alkaline earth aluminate fluorescent substance which activated this by Eu^{2+} or ***** (ed) by Eu^{2+} and Mn^{2+} By finding out presenting efficient luminescence and small blue luminescence of degradation with the passage of time, and using the mixed fluorescent substance which it comes to mix by the predetermined ratio to which this was restricted with the YOX red luminescence fluorescent substance and the LAP green luminescence fluorescent substance as a fluorescent screen This invention equipped with the header and the following configuration for the above-mentioned technical problem being solved was completed.

[0011] (1) General formula Alkaline earth aluminate fluorescent substance characterized by what it is expressed with $\text{Ba}_{1-x-y}\text{Sr}_x\text{Eu}_y\text{Mg}_{1-z}\text{Mn}_z$ aluminum 10O17, and is expressed with the number with which x in a formula, and y and z fill $0.4 \leq x \leq 0.6$, $0.03 \leq y \leq 0.3$, and the conditions that become $0 \leq z \leq 0.04$, respectively.

(2) General formula Alkaline earth aluminate fluorescent substance characterized by what it is expressed with $\text{Ba}_{1-x-y}\text{Sr}_x\text{Eu}_y\text{Mg}_{1-z}\text{Mn}_z$ aluminum 10O17, and is expressed with the number with which x in a formula, and y and z fill $0.4 \leq x \leq 0.6$, $0.075 \leq y \leq 0.225$, and the conditions that become $0 \leq z \leq 0.0225$, respectively.

[0012] (3) Above (1) Or (2) Fluorescent lamp characterized by using the alkaline earth aluminate fluorescent substance of a publication as a fluorescent substance layer of a glass tube wall.

(4) The above characterized by using the mixed fluorescent substance which contains the mixing ratio of an alkaline earth aluminate fluorescent substance, a YOX red luminescence fluorescent substance, and an LAP green luminescence fluorescent substance in 1:0.5-2.5:0.3-3.0 as said fluorescent substance layer (3) Fluorescent lamp of a publication.

[0013]

[Embodiment of the Invention] The alkaline earth aluminate fluorescent substance of this invention To stoichiometric each oxide or the compound which generates these oxides easily at an elevated temperature of Ba, Sr, Mg, aluminum, Eu, and Mn Empirical formula $\text{Ba}_{1-x-y}\text{Sr}_x\text{Eu}_y\text{Mg}_{1-z}\text{Mn}_z$ aluminum 10O17 It mixes at a rate which becomes (however, x in a formula, and y and z are the numbers which fulfill $0.4 \leq x \leq 0.6$, $0.03 \leq y \leq 0.3$, and the conditions that become $0 \leq z \leq 0.04$, respectively). By filling up a heat-resistant container and calcinating once or more over 2 - 40 hours at the temperature of 1200-1700 degrees C in a reducing atmosphere, the alkaline earth aluminate fluorescent substance of this invention activated by Eu^{2+} , or Eu^{2+} and Mn^{2+} is obtained.

[0014] In the alkaline earth aluminate fluorescent substance ($\text{Ba}_{1-x-y}\text{Sr}_x\text{Eu}_y\text{Mg}_{1-z}\text{Mn}_z$ aluminum 10O17) ***** (ed) by Eu^{2+} activation or Eu^{2+} , and Mn^{2+} of this invention For the purpose achievement of this invention, the amount range of the amount of permutations of Sr which permutes a part of Ba (x), the concentration (y) of Eu, and the concentration (z) of Mn Although it is desirable that it is in $0.4 \leq x \leq 0.6$, $0.03 \leq y \leq 0.3$, and $0 \leq z \leq 0.04$, respectively

When this x, and y and z are in $0.4 < x \leq 0.6$, $0.075 \leq y \leq 0.225$, and $0 \leq z < 0.025$, respectively, since fewer fluorescent substances of change of the luminescent color in the luminescence brightness list of the fluorescent substance obtained especially with time are obtained, it is desirable. In addition, since the concentration (y) of Eu in a fluorescent substance has the inclination for degradation by the heat in the baking process at the time of fluorescent lamp manufacture to become large when this increases, as for the concentration (y value) of Eu, carrying out to 0.3 or less is desirable [concentration].

[0015] When these fluorescent substances are used as a blue luminescence component fluorescent substance of the luminescence constituent of a fluorescent lamp, it becomes possible to offer a high color rendering and an efficient fluorescent lamp with little degradation with the passage of time from the case where Eu^{2+} and Mn^{2+} which are used as a blue luminescence fluorescent substance of the conventional fluorescent lamp use an activation barium strontium magnesium aluminate fluorescent substance.

[0016] Drawing 1 is what illustrates the emission spectrum when exciting the Eu^{2+} activation alkaline earth aluminate fluorescent substance of this invention, and the conventional Eu^{2+} activation alkaline earth aluminate fluorescent substance by 253.7nm ultraviolet rays, respectively. The curves a and b of drawing 1 $R > 1$ are one example of the fluorescent substance of this invention, respectively. As an Eu^{2+} activation barium strontium magnesium aluminate fluorescent substance ($\text{Ba}_{0.4}\text{Sr}_{0.5}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$) and a blue luminescence fluorescent substance of the conventional fluorescent lamp The Eu^{2+} activation barium magnesium aluminate fluorescent substance ($\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$) currently used is shown.

[0017] the peak location of luminescence which originates in Eu^{2+} compared with (the curve a of drawing 1), and the conventional barium magnesium aluminate fluorescent substance (the curve b of drawing 1) by permuting some barium of the conventional barium magnesium aluminate fluorescent substance with strontium so that the comparison of the curves a and b of drawing 1 may show -- a long wave -- while moving to a merit side, the luminescence reinforcement of 460-600nm becomes large.

[0018] Moreover, Curve a and Curve b of drawing 2 are the different Eu^{2+} activation alkaline earth aluminate fluorescent substance of this invention, respectively. Are used as the barium strontium magnesium aluminate fluorescent substance ($\text{Ba}_{0.4}\text{Sr}_{0.5}\text{Eu}_{0.1}\text{Mg}_{0.988}\text{Mn}_{0.012}\text{aluminum}_{10}\text{O}_{17}$) which ***** (ed) by Eu^{2+} and Mn^{2+} , and a blue luminescence fluorescent substance of the conventional fluorescent lamp. The emission spectrum when exciting the barium strontium magnesium aluminate fluorescent substance ($\text{Ba}_{0.6}\text{Sr}_{0.3}\text{Eu}_{0.1}\text{Mg}_{0.998}\text{Mn}_{0.012}\text{aluminum}_{10}\text{O}_{17}$) which ***** (ed) by Eu^{2+} and Mn^{2+} by 253.7nm ultraviolet rays, respectively It illustrates.

[0019] So that the comparison of the curves a and b of drawing 2 may show Conventional Eu^{2+} The barium strontium magnesium aluminate fluorescent substance (the curve a of drawing 2) which ***** (ed) by Eu^{2+} and Mn^{2+} of this invention compared with the barium strontium magnesium aluminate fluorescent substance (the curve b of drawing 2) which ***** (ed) by Mn^{2+} and the amount of the permutation by Sr While the peak location of luminescence which originates in Eu^{2+} by making [many] it moves to a long wavelength side Although the location of the luminescence peak resulting from Mn^{2+} does not change, since the luminescence reinforcement of 460-600nm becomes large, the relative intensity to the peak of luminescence resulting from Eu^{2+} becomes high.

[0020] Thus, the peak location of luminescence resulting from Eu^{2+} moves the alkaline earth aluminate fluorescent substance of this invention to a long wavelength side, and the luminescence reinforcement of further 460-600nm becomes large. This Eu^{2+} of this invention, and Mn^{2+} an activation barium strontium magnesium aluminate fluorescent substance The amount of permutations to Mn of Mg Eu^{2+} and Mn^{2+} which are used as a blue luminescence fluorescent substance of the conventional fluorescent lamp from an activation barium strontium magnesium aluminate fluorescent substance at least Or even if this amount of permutations is 0, the thing including the luminescence peak which originates in 515nm Mn^{2+} in the emission spectrum when exciting by 253.7nm ultraviolet rays for which relative intensity of 460-600nm luminescence can be made equivalent is meant.

[0021] Although the property improvement of the alkaline earth aluminate fluorescent substance ***** (ed) by Eu^{2+} or Eu^{2+} , and Mn^{2+} of this invention being high brightness, controlling decline in the luminous efficiency by heat [the conventional alkaline earth aluminate fluorescent substance / especially], and reducing fluctuation of the luminescent color with time is made By carrying out the section permutation of a part of Ba in fluorescent substance host crystal by Sr, since the location of the oxygen in the Ba-O layer under crystal was stable, the reason is considered.

[0022] On the other hand, the fluorescent lamp of this invention uses as a blue luminescence fluorescent substance the alkaline earth aluminate fluorescent substance ***** (ed) by Eu^{2+} activation or above-mentioned Eu^{2+} , and above-mentioned Mn^{2+} of this invention. To this, for example, the europium activation yttrium oxide fluorescent substance shown by $\text{Y}_{2-x}\text{Eu}_x\text{O}_3$ (however, x is a number which fulfills the conditions of $0.02 \leq x \leq 0.1$) of red luminescence (henceforth a "YOX fluorescent substance"), $\text{La}_{1-y-z}\text{Ce}_y\text{Tb}_z\text{PO}_4$ (however) of green luminescence the number with which y and z fill the conditions of $0.1 \leq y \leq 0.6$ and $0.1 \leq z \leq 0.3$, respectively -- it is -- the cerium and terbium which are shown with a binder the mixed fluorescent substance which mixed the activation phosphoric acid lanthanum

fluorescent substance (henceforth an "LAP fluorescent substance") by the predetermined quantitative ratio After mixing, considering as a fluorescent substance slurry and applying this to the wall of a glass tube, a high color rendering and a fluorescent lamp with little degradation can be offered efficient by manufacturing a fluorescent lamp by the approach generally learned. Although the mixed weight ratio of the blue luminescence fluorescent substance (aluminate fluorescent substance) and red luminescence fluorescent substance (YOX) in the fluorescent lamp of this invention, and a green luminescence fluorescent substance (LAP) changes with color temperatures of a request of the obtained fluorescent lamp When light is made to emit, in order to present luminescence of the range which can be called white A color temperature assumes about 4000-8000K to raise especially whenever [color rendering]. blue -- fluorescent substance:red fluorescent substance: -- each mixed weight ratio of a green fluorescent substance that what is necessary is just to be in the range of 1:0.5-2.5:0.3-3.0 It is desirable to consider as the range of 1:0.7-2.0:0.3-3.0 which was able to balance the amount of mixing of 3 color fluorescent substance.

[0023] in addition -- although the alkaline earth fluorescent substance of this invention permutes a part of Ba by Sr -- the amount of permutations of Sr at that time -- (-- in case a fluorescent lamp is manufactured using this fluorescent substance by making x) into increase and the permutation range of $0.4 \leq x \leq 0.6$, it also has the effectiveness that degradation by the heat in a baking process becomes small, and it becomes possible to offer an efficient fluorescent lamp.

[0024]

[Example]

(Example 1)

BaCO₃ 0.4 mol SrCO₃ 0.5 mol Eu₂O₃ 0.05 mol 3MgCO(s)₃ and Mg₂(OH) 0.245 mol MnO₂ 0.02 mol gamma type-aluminum 2O₃ 5.0 mol The AlF₃ 0.010 (flux) mol above-mentioned raw material was fully mixed, crucible was filled up, and the lump of a graphite was further picked up on the raw material, and it calcinated over 24 hours including rising-and-falling-temperature time amount at 1450 degrees C of maximum temperatures, having covered and carrying out aeration of the mixed gas of nitrogen and a small amount of hydrogen. Subsequently, distribution, washing, desiccation, and processing of screen analysis were performed for baking powder, and Eu²⁺ of an example 1 and Mn²⁺ obtained the barium strontium magnesium aluminate blue luminescence fluorescent substance (Ba_{0.4} Sr_{0.5} Eu_{0.1} Mg_{0.98}Mn_{0.02}aluminum 10O₁₇) of activation.

[0025] Thus, a luminescence wavelength peak is 460nm and, as for the luminescent color when exciting the blue luminescence fluorescent substance of the acquired example 1 by 253.7nm ultraviolet rays, the luminescent chromaticity point showed blue luminescence of $x = 0.143$ and $y = 0.187$. When it excited by 253.7nm ultraviolet rays after heat-treating this blue fluorescent substance for 15 minutes at 650 degrees C of maximum temperatures in the air ambient atmosphere and cooling to a room temperature after that, the ratio (brightness maintenance factor at the time of heat treatment) of the luminous efficiency after heat treatment to before heat treatment is 98.8%, and was understood that the heat-resistant hysteresis nature to baking processing is very good.

[0026] Next, apply this blue fluorescent substance to a glass bulb inside, and the fluorescent lamp (floor line20S) of blue monochrome luminescence is manufactured. After turning this on for 1000 hours, a fluorescent substance is removed from the tube wall of a lamp. The luminescent color (X', Y') when exciting by 253.7nm ultraviolet rays is $x' = 0.145$ and $y' = 0.190$. The difference (difference of the luminescent chromaticity by use) of the luminescent chromaticity point of a fluorescent substance before and after using this fluorescent substance as a fluorescent screen of a lamp was a value with the very small chromaticity difference of $\Delta x = 0.002$, $\Delta y = 0.003$, and the fluorescent substance before and behind use.

[0027]

(Example 1 of a comparison)

BaCO₃ 0.6 mol SrCO₃ 0.3 mol Eu₂O₃ 0.05 mol 3MgCO(s)₃ and Mg₂(OH) 0.245 mol MnO₂ 0.02 mol gamma type-aluminum 2O₃ 5.0 mol It is made to be the same as that of the blue luminescence fluorescent substance of an example 1 except having used the above-mentioned raw material as an AlF₃ 0.010 (flux) mol fluorescent substance raw material. Eu²⁺ and Mn²⁺ of the example 1 of a comparison obtained the activation barium strontium magnesium aluminate blue luminescence fluorescent substance (Ba_{0.6} Sr_{0.3}Eu_{0.1} Mg_{0.98}Mn_{0.02}aluminum 10O₁₇).

[0028] Thus, a luminescence wavelength peak is 450nm and, as for the luminescent color when exciting the blue luminescence fluorescent substance of the acquired example 1 of a comparison by 253.7nm ultraviolet rays, the luminescent chromaticity point showed blue luminescence of $x = 0.144$ and $y = 0.153$. When asked for the ratio (brightness maintenance factor at the time of heat treatment) of the luminous efficiency after heat treatment to before heat treatment when heat-treating this fluorescent substance like an example 1, it was 85.5% and the heat-resistant hysteresis nature to baking processing was bad.

[0029] The fluorescent lamp (floor line20S) of blue monochrome luminescence is manufactured like an example 1 further again using this blue fluorescent substance. After switching on the light like an example 1 for 1000 hours, a fluorescent substance is removed from the tube wall of a lamp. The luminescent color (X', Y') when exciting by

253.7nm ultraviolet rays was $x'=0.145$ and $y'=0.155$, and the differences (Δx , Δy) of the luminescent chromaticity point of a fluorescent substance before and after using this fluorescent substance as a lamp were $\Delta x=0.001$ and $\Delta y=0.002$.

[0030] To Table 1 and 2, the fluorescent substance presentation of the blue luminescence fluorescent substance of an example 1 and the example 1 of a comparison, and the luminescent color (an emission peak wavelength and a luminescent chromaticity point ** color (x y) --) of said fluorescent substance The ratio of the luminous efficiency after heat treatment to before heat treatment (brightness maintenance factor at the time of heat treatment), After carrying out lighting use of the fluorescent lamp using this fluorescent substance as a fluorescent screen of a lamp for 1000 hours, Luminescent chromaticity point [of a fluorescent substance] ** (x' , y') which exfoliated and collected fluorescent screens and the difference of the luminescent chromaticity of a fluorescent substance before and after using it as a fluorescent screen of a lamp (Δx , Δy), i.e., the difference of the luminescent chromaticity by use, (**-**) were shown, respectively.

[0031] (Examples 2-28) Eu^{2+} of examples 2-28 and Mn^{2+} manufactured the barium strontium magnesium aluminate blue luminescence fluorescent substance of activation like the blue luminescence fluorescent substance of an example 1 except having mixed so that it might become each presentation which showed each fluorescent substance raw material of an example 1 in Table 1 and 2. Thus, the luminescent color {emission peak wavelength when exciting the presentations of each obtained blue luminescence fluorescent substance of examples 2-28, and these fluorescent substances by 253.7nm ultraviolet rays, The time of heat-treating luminescent chromaticity point **(x y)} and these fluorescent substances like an example 1, The ratio of the luminous efficiency after heat treatment to before heat treatment (brightness maintenance factor at the time of heat treatment), The fluorescent lamp (floor line20S) of blue monochrome luminescence is manufactured like an example 1 using each of these blue fluorescent substances, respectively. After switching on the light like an example 1 for 1000 hours, a fluorescent substance is removed from the tube wall of a lamp. luminescent chromaticity [of the fluorescent substance when exciting by 253.7nm ultraviolet rays] ** {the luminescent chromaticity point after use (x' , y')}, and the difference (Δx , Δy) of the luminescent chromaticity of the fluorescent substance by use -- that is, (**-**), it was shown in Table 1 and 2, respectively.

[0032]

[Table 1]

No.	行色螢光体		励起時の印痕維持率	使用後の発光色度(②)		使用による発光色度の差(②-①)			
	螢光体組成	発光色		x'	y'	Δx	Δy		
		ピーク波長(nm)						発光色座点(①)	
実施例1	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.143	0.187	98.8	0.145	0.190	0.002	0.003
実施例2	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.145	0.176	96.1	0.147	0.179	0.002	0.003
実施例3	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.145	0.161	95.8	0.146	0.163	0.001	0.002
実施例4	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.144	0.145	95.5	0.145	0.147	0.001	0.002
実施例5	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.146	0.124	97.0	0.147	0.126	0.001	0.002
実施例6	Ba ₂ MgSi ₂ Al ₂ O ₁₇	460	0.145	0.114	92.9	0.146	0.116	0.001	0.002
実施例7	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.145	0.216	98.6	0.146	0.219	0.001	0.003
実施例8	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.145	0.200	98.9	0.146	0.204	0.001	0.004
実施例9	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.143	0.186	98.9	0.145	0.189	0.002	0.003
実施例10	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.146	0.171	98.4	0.147	0.174	0.001	0.003
実施例11	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.144	0.153	97.8	0.145	0.156	0.001	0.003
実施例12	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.143	0.138	99.0	0.145	0.141	0.002	0.003
実施例13	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	460	0.143	0.118	96.9	0.144	0.121	0.001	0.003
実施例14	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO	460	0.145	0.104	95.5	0.146	0.106	0.001	0.002
実施例15	Ba ₂ MgSi ₂ Al ₂ O ₁₇ :MgO, 0.01Mn ²⁺	455	0.144	0.202	97.9	0.146	0.206	0.002	0.004

[0033]

[Table 2]

No.	青 色 蛍 光 体 組 成	発 光 色		熱処理時の輝度維持率 (%)	使用後の発光色度 (②)		使用による発光色度の差 (②-①)		
		ピーク波長 (nm)	発光色度点(①)		x'	y'	Δx	Δy	
			x						y
実施例16	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.983} Mn _{0.017} Al ₁₀ O ₁₇	455	0.144	0.179	99.1	0.146	0.183	0.002	0.004
実施例17	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.983} Mn _{0.017} Al ₁₀ O ₁₇	455	0.144	0.165	98.5	0.145	0.168	0.001	0.003
実施例18	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.988} Mn _{0.012} Al ₁₀ O ₁₇	455	0.145	0.149	97.9	0.147	0.152	0.002	0.003
実施例19	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.993} Mn _{0.008} Al ₁₀ O ₁₇	455	0.145	0.134	97.2	0.146	0.136	0.001	0.002
実施例20	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.997} Mn _{0.003} Al ₁₀ O ₁₇	455	0.146	0.11	98.4	0.148	0.113	0.002	0.003
実施例21	Ba _{0.5} Sr _{0.4} Eu _{0.1} MgAl ₁₀ O ₁₇	460	0.145	0.102	96.9	0.147	0.104	0.002	0.002
比較例22	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.975} Mn _{0.025} Al ₁₀ O ₁₇	460	0.147	0.214	97.5	0.148	0.216	0.001	0.002
実施例23	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.99} Mn _{0.01} Al ₁₀ O ₁₇	460	0.147	0.203	98.2	0.148	0.205	0.001	0.002
実施例24	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.983} Mn _{0.017} Al ₁₀ O ₁₇	450	0.147	0.187	97.9	0.148	0.189	0.001	0.002
実施例25	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.988} Mn _{0.012} Al ₁₀ O ₁₇	460	0.148	0.172	97.8	0.149	0.174	0.001	0.002
実施例26	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.992} Mn _{0.008} Al ₁₀ O ₁₇	460	0.147	0.156	97.2	0.148	0.158	0.001	0.002
実施例27	Ba _{0.5} Sr _{0.4} Eu _{0.1} Mg _{0.997} Mn _{0.003} Al ₁₀ O ₁₇	460	0.146	0.137	97.6	0.147	0.139	0.001	0.002
実施例28	Ba _{0.5} Sr _{0.4} Eu _{0.1} MgAl ₁₀ O ₁₇	460	0.146	0.128	97.1	0.147	0.13	0.001	0.002
比較例 1	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	450	0.144	0.153	85.5	0.145	0.155	0.001	0.002

[0034] The barium strontium magnesium aluminate blue luminescence fluorescent substance (Ba_{0.4} Sr_{0.5} Eu_{0.1} Mg_{0.98} Mn_{0.02} aluminum 10O₁₇) of activation of Eu²⁺ of an example 1, and Mn²⁺ 30.6 % of the weight, (Example 29) an empirical formula -- Y_{1.92}E_{0.08}O₃ it is -- a YOX red luminescence fluorescent substance 37.2% of the weight an empirical formula -- La_{0.55}Ce_{0.30}Tb_{0.15}PO₄ it is -- 32.2 % of the weight for an LAP green luminescence fluorescent substance It fully mixed with the lacquer of a nitrocellulose to butyl acetate, and the fluorescent substance slurry was produced, and after applying to the glass tube and drying, the three-wave fluorescent lamp (floor line20S) which is color temperature 5000K of an example 29 was manufactured by the usual approach. Thus, the initial property of the obtained fluorescent lamp was 99.5 in the relative value when setting the lamp light bundle of the fluorescent lamp of the following example 2 of a comparison to 100, and the average color-rendering-properties characteristic Ra was 90.1 (Table 3).

[0035] (Example 2 of a comparison) For a comparison Replace with the blue fluorescent substance of the above-mentioned example 1 as a blue fluorescent substance, and Eu²⁺ and Mn²⁺ of the example 1 of a comparison use an activation barium strontium magnesium aluminate blue luminescence fluorescent substance (Ba_{0.6} Sr_{0.3} Eu_{0.1} Mg_{0.98} Mn_{0.02} aluminum 10O₁₇). The three-wave fluorescent lamp (floor line20S) of the example 2 of a comparison as well as the three-wave fluorescent lamp of the above-mentioned example 29 was manufactured except having considered the mixed weight ratio of each color fluorescent substance as the passage of Table 3. The relative value of the flux of light and the average color-rendering-properties characteristic Ra immediately after lighting of the three-wave fluorescent lamp of these examples 29 and the example 2 of a comparison were shown in Table 3.

[0036] (Examples 30-56) The three-wave fluorescent lamp of examples 30-56 as well as the fluorescent lamp of an example 29 was manufactured except having used the mixed fluorescent substance which mixed each blue luminescence fluorescent substance of examples 2-28, the LAP green luminescence fluorescent substance used in the example 29, and the YOX red luminescence fluorescent substance again by the mixed weight ratio shown in Table 2, respectively. The relative value of the flux of light immediately after lighting of each obtained fluorescent lamp and the average color-rendering-properties characteristic Ra were measured, and it was shown in Table 3.

[0037]

[Table 3]

実施例 (比較例)	各色蛍光体とその混合比 (重量%)			光 束 (相対値)	平均演色 価数 (R a)
	実施例1の 青色蛍光体	Y O X 赤色蛍光体	L A P 緑色蛍光体		
実施例29	30.6	37.2	32.2	99.5	90.1
実施例30	29.3	36.9	33.8	100.4	90.4
実施例31	28.3	36.1	35.6	100.7	90.4
実施例32	27.3	35.2	37.5	101.0	89.9
実施例33	26.1	34.2	39.7	101.3	89.2
実施例34	26.0	33.5	40.5	101.0	88.7
実施例35	32.4	39.4	28.2	99.1	89.5
実施例36	31.1	37.8	31.1	100.0	89.6
実施例37	30.1	37.0	32.9	100.3	89.9
実施例38	28.9	36.1	35.0	100.9	89.9
実施例39	28.0	35.1	36.9	100.9	89.5
実施例40	26.9	34.4	38.7	101.4	89.2
実施例41	25.6	33.5	40.9	101.9	88.3
実施例42	24.7	32.9	42.4	102.0	87.6
実施例43	31.4	38.5	30.1	99.4	89.8
実施例44	30.0	36.9	33.1	99.8	89.7
実施例45	28.8	36.2	35.0	100.4	89.7
実施例46	27.9	35.3	36.8	100.6	89.4
実施例47	26.7	34.6	38.7	101.3	88.9
実施例48	25.7	33.4	40.9	101.2	87.8
実施例49	25.1	33.0	41.9	101.5	87.3
実施例50	32.6	39.0	28.4	99.0	89.7
実施例51	31.4	38.4	30.2	99.6	90.2
実施例52	30.4	37.4	32.2	100.0	90.6
実施例53	29.3	36.6	34.1	100.3	90.9
実施例54	28.0	35.8	36.2	100.9	90.7
実施例55	26.8	34.8	38.4	101.4	90.2
実施例56	26.4	34.3	39.3	101.3	89.8
比較例 2	26.6	35.6	37.8	100.0	88.6

[0038] As compared with the fluorescent lamp of the example 2 of a comparison which used the blue fluorescent substance of the same europium concentration, the fluorescent lamp (examples 29-56) of the flux of light of this invention was almost the same, its average color-rendering-properties characteristic (Ra) was improving, color rendering properties have been improved more, or the average color-rendering-properties characteristic (Ra) was almost equivalent, the flux of light was improving, and luminous efficiency has been improved so that clearly from Table 3. Especially, as compared with the fluorescent lamp of the example 2 of a comparison, the flux of light and the average color-rendering-properties characteristic of both the fluorescent lamps of examples 30-34, examples 36-40, examples 45-47, and examples 52-56 were improving, and both color rendering properties and luminous efficiency have been improved.

[0039] Moreover, although not illustrated in front Naka, it was checked that degradation with the passage of time according [the fluorescent lamp of examples 29-56] to continuation lighting compared with the example 2 of a comparison is also improved. Also in these, the degree of an improvement of degradation with the passage of time under fluorescent lamp lighting of examples 29-33, examples 36-41, examples 44-48, and examples 51-55 was size [especially / the fluorescent lamp of the example 2 of a comparison and an example 34, an example 35, an example 42 an example 43, an example 49, an example 50, and an example 56].

[0040] Further Each blue luminescence fluorescent substance of examples 1-28 and the example 1 of a comparison, (Examples 57-84, example 3 of a comparison) It is made to be the same as that of the fluorescent lamp of an example 29 except using for a YOX red luminescence fluorescent substance list the mixed fluorescent substance which comes to mix an LAP green luminescence fluorescent substance by the weight ratio indicated to Table 4, respectively as a fluorescent screen. The three-wave fluorescent lamp of color temperature 6500K of examples 57-84 and the example 3 of a comparison (floor line20S) was manufactured. Thus, about the obtained fluorescent lamp, the result of having measured the initial flux of light (relative value) and the average color rendering characteristic (Ra) immediately after lighting was shown in Table 4.

[Table 4]

実施例 (比較例)	使用した蛍光体種とその混合比 (重量%)						光 束 (相対値)	平均演色 価数(Ra)
	青色蛍光体	赤色蛍光体	緑色蛍光体					
実施例57	実施例 1	41.4	Y O X	32.6	L A P	26.0	99.3	90.2
実施例58	" 2	39.8	"	32.1	"	28.1	100.5	91.0
実施例59	" 3	38.4	"	31.0	"	30.6	101.0	91.8
実施例60	" 4	37.1	"	29.7	"	33.2	101.4	92.2
実施例61	" 5	35.5	"	28.3	"	36.2	101.8	81.5
実施例62	" 6	35.2	"	37.5	"	37.3	101.4	90.9
実施例63	" 7	43.7	"	35.6	"	20.7	98.8	86.5
実施例64	" 8	42.0	"	33.5	"	24.5	100.0	88.8
実施例65	" 9	40.7	"	32.4	"	26.9	100.3	90.1
実施例66	" 10	39.1	"	31.2	"	29.7	101.2	90.9
実施例67	" 11	37.9	"	29.7	"	32.4	101.2	91.5
実施例68	" 12	36.5	"	28.7	"	34.8	101.8	91.4
実施例69	" 13	34.8	"	27.6	"	37.6	102.5	90.5
実施例70	" 14	33.6	"	26.7	"	39.7	102.7	89.4
実施例71	" 15	42.4	"	34.4	"	23.2	99.2	88.1
実施例72	" 16	40.5	"	32.2	"	27.3	100.0	90.2
実施例73	" 17	39.1	"	31.2	"	29.7	100.6	90.9
実施例74	" 18	37.9	"	29.9	"	32.2	100.8	91.5
実施例75	" 19	36.3	"	29.0	"	34.7	101.7	91.2
実施例76	" 20	34.9	"	27.2	"	37.9	101.7	89.9
実施例77	" 21	34.2	"	26.7	"	39.1	102.1	89.1
実施例78	" 22	44.0	"	35.0	"	21.0	98.7	87.4
実施例79	" 23	42.5	"	34.2	"	23.3	99.6	88.9
実施例80	" 24	41.1	"	32.8	"	26.1	100.0	90.6
実施例81	" 25	39.7	"	31.7	"	28.6	100.5	91.8
実施例82	" 26	38.0	"	30.6	"	31.4	101.2	92.5
実施例83	" 27	36.4	"	29.3	"	34.3	101.9	92.6
実施例84	" 28	35.9	"	28.5	"	35.6	101.8	92.1
比較例 2	比較例 1	36.2	"	30.2	"	33.6	100.0	89.9

[0042] As compared with the fluorescent lamp of the example 3 of a comparison which used the blue fluorescent substance of the europium concentration with the same fluorescent lamp (examples 57-84) of this invention, the flux of light was almost the same, and the average color-rendering-properties characteristic (Ra) was improving, color rendering properties have been improved more, or the average color-rendering-properties characteristic (Ra) was almost equivalent, the flux of light was improving, and luminous efficiency has been improved so that clearly from Table 4. Especially, as compared with the fluorescent lamp of the example 3 of a comparison, the flux of light and the average color-rendering-properties characteristic Ra of both the fluorescent lamps of examples 58-62, examples 65-69, examples 72-76, and examples 80-84 improved, and both color rendering properties and luminous efficiency have been improved.

[0043] (An example 85, example 4 of a comparison) The blue fluorescent substance (Ba0.3 Sr0.5 Eu0.2Mg0.98Mn0.02aluminum 10O17) of an example 85 and the blue fluorescent substance (Ba0.7 Sr0.1 Eu0.2 Mg0.986 Mn0.014 aluminum 10O17) of the example 4 of a comparison were manufactured like the example 1. Thus, presentation [of the blue fluorescent substance of the acquired example 85 and the example 4 of a comparison], emission-peak-wavelength, and luminescent chromaticity ** (x y) was shown in Table 5.

[0044] Next, the blue fluorescent substance of an example 85 and the blue fluorescent substance (said fluorescent substance presentation, the emission peak wavelength, and the luminescent chromaticity point were shown in Table 5) of the example 4 of a comparison were mixed with the YOX red fluorescent substance and the LAP green fluorescent substance at a mixed rate shown in Table 6, the mixed fluorescent substance was prepared, and the three-wave region luminescence form fluorescent lamp of color temperature 5000K and floor line20S was produced about the fluorescent substance of an example 85 and the example 4 of a comparison like the example 29. About each obtained fluorescent lamp, the initial flux of light (relative value) and the average color rendering characteristic (Ra) of the mixed rate (% of the weight) of each color fluorescent substance used as a fluorescent screen and the obtained fluorescent lamp were measured, and the result was shown in Table 6.

[0045]

[Table 5]

No.	青色発光蛍光体				
	蛍光体組成			ピーク波長 (nm)	
				発光色度点	
				x	y
実施例 57	$\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Eu}_{0.02}\text{Mn}_{0.02}\text{Al}_{1.0}\text{O}_{1.7}$			460	0.142
比較例 3	$\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Eu}_{0.02}\text{Mn}_{0.014}\text{Al}_{1.0}\text{O}_{1.7}$			455	0.169

[0046]

[Table 6]

No.	蛍光ランプ				
	蛍光体種と混合比 (重量%)			初期光束 (相対値)	平均演色 偏数 (Ra)
	青色蛍光体	赤色蛍光体	緑色蛍光体		
実施例 57	実施例 57 蛍光体 32.2	Y O X 39.4	L A P 28.4	100.3	92.1
比較例 3	比較例 40 蛍光体 28.0	Y O X 35.9	L A P 36.1	100.0	89.1

[0047] As compared with the fluorescent lamp of the example 4 of a comparison which used the blue fluorescent substance of the europium concentration with the same fluorescent lamp of this invention of an example 85, the average color-rendering-properties characteristic (Ra) of the flux of light was improving highly, and both color rendering properties and luminous efficiency have been improved more so that clearly from Table 6.

[0048]

[Effect of the Invention] The peak location of luminescence which originates in europium in the emission spectrum when exciting conventional Eu and conventional Mn by 253.7nm ultraviolet rays by adopting the above-mentioned configuration compared with the alkaline earth aluminate fluorescent substance of a with moves this invention to a long wavelength side. When the luminescence reinforcement of further 460-600nm becomes large and used it as a fluorescent substance of the blue luminescence component of a three-wave fluorescent lamp especially, the high color rendering and the efficient three-wave region luminescence form fluorescent lamp with little change of the luminescent color under lamp lighting and degradation with the passage of time could be offered.

[Translation done.]

(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号

特開2000-109826

(P2000-109826A)

(43)公開日 平成12年4月18日(2000.4.18)

(51)Int.Cl. ⁷	識別記号	F I	テマコード(参考)
C 0 9 K 11/64	CPM	C 0 9 K 11/64	4 H 0 0 1
11/80	CPM	11/80	5 C 0 4 3
H 0 1 J 61/44		H 0 1 J 61/44	N

審査請求 未請求 請求項の数2 O L (全 10 頁)

(21)出願番号 特願平10-282311
(22)出願日 平成10年10月5日(1998.10.5)

(71)出願人 390019976
化成オプトニクス株式会社
神奈川県小田原市成田1060番地
(72)発明者 大塚 礼治
神奈川県小田原市成田1060番地 化成オ
プトニクス株式会社内
(72)発明者 石井 浩文
神奈川県小田原市成田1060番地 化成オ
プトニクス株式会社内
(74)代理人 100072844
弁理士 萩原 亮一 (外2名)

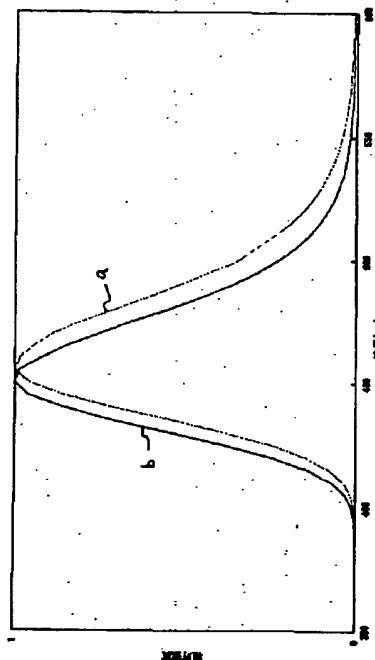
最終頁に続く

(54)【発明の名称】 アルカリ土類アルミン酸塩蛍光体及び蛍光ランプ

(57)【要約】

【課題】 高演色、高効率でかつ蛍光ランプ点灯中の発光色の変化、及び発光効率の経時劣化の小さい蛍光体、並びに蛍光ランプを提供するしようとするものである。

【解決手段】 一般式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ で表され、式中の x 、 y 及び z がそれぞれ $0.4 \leq x \leq 0.6$ 、 $0.03 \leq y \leq 0.3$ 及び $0 \leq z \leq 0.04$ なる条件を満たす数で表されることを特徴とするアルカリ土類アルミン酸塩蛍光体、及び該蛍光体を用いた蛍光ランプである。



【特許請求の範囲】

【請求項1】 一般式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ で表され、式中の x 、 y 及び z がそれぞれ $0.4 \leq x \leq 0.6$ 、 $0.03 \leq y \leq 0.3$ 及び $0 \leq z \leq 0.04$ なる条件を満たす数で表されることを特徴とするアルカリ土類アルミン酸塩蛍光体。

【請求項2】 請求項1記載のアルカリ土類アルミン酸塩蛍光体を用いてガラス管内壁の蛍光体層を形成してなることを特徴とする蛍光ランプ。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、2価のユーロピウム (Eu^{2+}) で付活するか、2価のユーロピウム (Eu^{2+}) と2価のマンガン (Mn^{2+}) とで共付活したアルカリ土類アルミン酸塩蛍光体、及びこの蛍光体を青色発光成分の蛍光膜として用いた3波長域発光型蛍光ランプに関する。

【0002】

【従来の技術】 近年、一般照明用蛍光ランプの分野で、3波長域発光型蛍光ランプ（以下、単に、「蛍光ランプ」という）が開発されて実用に供されている。この蛍光ランプに使用される蛍光体は、比較的狭帯域の発光スペクトル分布を有する赤色、緑色、青色の3種の蛍光体を適当な割合で混合したものである。

【0003】 この蛍光ランプに使用される蛍光体は、赤色蛍光体として3価のユーロピウム (Eu^{3+}) 付活の酸化イットリウム、緑色蛍光体としてセリウム (Ce) 及びテルビウム (Tb) 付活の燐酸ランタン、青色蛍光体としてアルカリ土類クロロ燐酸塩又は2価のユーロピウム (Eu^{2+}) 付活のバリウムマグネシウムアルミン酸塩がそれぞれ使用されている。

【0004】 この蛍光ランプは、光束、演色性の両面で優れており、平均演色評価数 (Ra) が84で、光束は例えば、直管型蛍光ランプの、FL20SSEX-N/18では1470ルーメン (1m) を実現している。さらに、上記3種の蛍光体に、青緑色、あるいは青緑色と深赤色の蛍光体を加え、4種あるいは5種の蛍光体を混合することにより、平均演色評価数 $Ra \geq 87$ を実現した蛍光ランプが実用されるようになった。また、特開平5-302082号公報では、青色成分である Eu^{2+} 付活アルカリ土類クロロ燐酸塩蛍光体の組成及び発光色を特定することにより、3種のみの蛍光体の混合によっても平均演色評価数 $Ra \geq 87$ の蛍光ランプが実現されるようになった。

【0005】 一方、青色成分として Eu^{2+} 付活バリウム・マグネシウムアルミン酸塩蛍光体を使用した蛍光ランプに関しては、 Eu^{2+} 付活バリウム・マグネシウムアルミン酸塩蛍光体に Mn^{2+} を共付活することによって演色性を向上させたものが実用化されている。また、特開昭56-86892号公報には、 $Ba_{1-x-y}Sr_xMg_y$

$Al_qO_{(1+p+q)/2q} : Eu^{2+}_y$ (ここで、 $0 < x \leq 0.1$ 、 $0.01 \leq y \leq 0.4$ 、 $0.8 \leq p \leq 4.0$ 、 $1.0 \leq q \leq 3.0$) で表される蛍光体を用いることにより、平均演色評価数 $Ra = 89$ を実現できると記載されている。

【0006】 ところで、青色成分として Eu^{2+} 付活のバリウム・マグネシウムアルミン酸塩蛍光体を使用した蛍光ランプは、 Eu^{2+} 付活アルカリ土類クロロ燐酸塩蛍光体を用いた蛍光ランプより光束が高くなるが、蛍光体の劣化による蛍光ランプの発光色の経時変化（カラーシフト）が大きいという問題もあった。この問題を解決する方法として、極めて限られた組成の Eu^{2+} 、又は Eu^{2+} と Mn^{2+} とで付活したアルカリ土類アルミン酸塩蛍光体を Eu^{3+} 付活酸化イットリウム（以下、「YOX赤色蛍光体」という）、及び Tb と Ce で共付活した燐酸ランタン（以下、「LAP緑色蛍光体」という）を限られた混合比率で混合して使用することが、特開平4-106187号公報や特開平4-106188号公報で提案されている。

【0007】 さらに、特開平3-106988号公報には、 $(Ba_{1-x-y}Sr_xM_y)O \cdot a(Mg_{1-p-q}Mn_pZn_q)O \cdot bAl_2O_3$ (ここで M は Sr 及び Ca のうちの少なくとも1種の元素を表し、式中の a 、 b 、 x 、 y 、 p 、 q は $a+3 \leq b \leq 4a+(3/2)$ 、 $(7/3)a-1 \leq b \leq (11/9)a+(17/3)$ 、 $0 < x \leq 0.4$ 、 $0 \leq y \leq 0.4$ 、 $0 < x+y \leq 0.4$ 、 $0.001 < (ap/x) \leq 0.2$ 、 $0 \leq q \leq 0.3$ 、 $0 \leq p+q \leq 0.3$) で表される蛍光体を上記と同じ目的で用いることが提案されている。

【0008】 しかし、これらのアルミン酸塩蛍光体や燐酸塩蛍光体を用いた蛍光ランプよりも、より一層高演色、高効率でかつ発光色の経時劣化によるカラーシフトの少ない蛍光ランプの実現が望まれている。従来から高演色性蛍光ランプ用の青色発光蛍光体として用いられてきたアルミン酸塩蛍光体は発光効率も高く、これを蛍光ランプに用いた場合、平均演色評価数 (Ra) の比較的良好な蛍光ランプとなし得るが、特に、 Mn を付活剤として含むアルミン酸塩蛍光体の場合、 Mn の添加量を増すことにより、これを蛍光ランプに用いた場合、ランプの平均演色評価数 (Ra) を高めることは可能であるが、その場合、効率（白色光を発する時の光束）は低くなり好ましくない。それ故、アルミン酸塩蛍光体にあっても、これを高演色性蛍光ランプ用の青色発光蛍光体として使用した場合、ランプの平均演色評価数 (Ra) 及び発光効率が共に高い蛍光体となり得るようなアルミン酸塩蛍光体の開発が望まれている。

【0009】

【発明が解決しようとする課題】 そこで、本発明は、従来の Eu^{2+} 付活、又は Eu^{2+} と Mn^{2+} 共付活のアルカリ土類アルミン酸塩蛍光体において、上記欠点を解消し、

高演色、高効率でかつ蛍光ランプ点灯中の発光色の変化、及び発光効率の経時劣化の小さい蛍光体、並びに蛍光ランプを提供するしようとするものである。

【0010】

【課題を解決するための手段】本発明者等は、上記課題の解決のために、蛍光ランプに使用されるアルカリ土類蛍光体の組成について更に詳細に検討した結果、アルカリ土類アルミン酸塩蛍光体の母体中のストロンチウム（Sr）の含有量が従来から使用されているアルカリ土類アルミン酸塩蛍光体よりも多い組成領域の蛍光体を高演色性蛍光ランプ用の青色発光蛍光体として使用した場合、この蛍光体のMnの付活量を少なくしても、また、Mnを共付活しない場合でも、より高いRa値と発光効率を示すことが分かった。即ち、バリウム（Ba）及びマグネシウム（Mg）を含むEu²⁺付活のアルカリ土類アルミン酸塩蛍光体のバリウム（Ba）の1部をストロンチウム（Sr）によって所定量置換し、さらに必要に応じてマグネシウム（Mg）の1部をマンガン（Mn）によって所定量置換して、蛍光体を構成する（Ba+Sr+Eu）成分：（Mg+Mn）成分：Al成分の各元素の比を1：1：10として、これをEu²⁺で付活するか、又はEu²⁺とMn²⁺とで共付活したアルカリ土類アルミン酸塩蛍光体について、高効率の発光と経時劣化の小さい青色発光を呈することを見だし、これをYOX赤色発光蛍光体やLAP緑色発光蛍光体と共に限られた所定の比率で混合してなる混合蛍光体を蛍光膜として使用することにより、上記課題が解決することを見出し、下記構成を備えた本発明を完成させた。

【0011】(1) 一般式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ で表され、式中のx、y及びzがそれぞれ $0.4 \leq x \leq 0.6$ 、 $0.03 \leq y \leq 0.3$ 及び $0 \leq z \leq 0.04$ なる条件を満たす数で表されることを特徴とするアルカリ土類アルミン酸塩蛍光体。

(2) 一般式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ で表され、式中のx、y及びzがそれぞれ $0.4 < x \leq 0.6$ 、 $0.075 \leq y \leq 0.225$ 及び $0 \leq z \leq 0.0225$ なる条件を満たす数で表されることを特徴とするアルカリ土類アルミン酸塩蛍光体。

【0012】(3) 前記(1)又は(2)記載のアルカリ土類アルミン酸塩蛍光体をガラス管内壁の蛍光体層として用いたことを特徴とする蛍光ランプ。

(4) 前記蛍光体層として、アルカリ土類アルミン酸塩蛍光体、YOX赤色発光蛍光体、及びLAP緑色発光蛍光体の混合比を1：0.5～2.5：0.3～3.0の範囲で含有する混合蛍光体を用いたことを特徴とする前記(3)記載の蛍光ランプ。

【0013】

【発明の実施の形態】本発明のアルカリ土類アルミン酸塩蛍光体は、Ba、Sr、Mg、Al、Eu及びMnの各酸化物又は高温で容易にこれらの酸化物を生成する化

合物を化学量論的に組成式 $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ （但し、式中のx、y及びzがそれぞれ $0.4 \leq x \leq 0.6$ 、 $0.03 \leq y \leq 0.3$ 及び $0 \leq z \leq 0.04$ なる条件を満たす数である）となる割合で混合し、耐熱容器に充填して還元性雰囲気中で1200～1700℃の温度で2～40時間かけて1回以上焼成することにより、Eu²⁺、又はEu²⁺とMn²⁺で付活した本発明のアルカリ土類アルミン酸塩蛍光体が得られる。

【0014】本発明のEu²⁺付活もしくはEu²⁺とMn²⁺とで共付活されたアルカリ土類アルミン酸塩蛍光体（ $Ba_{1-x-y}Sr_xEu_yMg_{1-z}Mn_zAl_{10}O_{17}$ ）において、本発明の目的達成のためには、Baの一部を置換するSrの置換量（x）、Euの濃度（y）及びMnの濃度（z）の量範囲は、それぞれ $0.4 \leq x \leq 0.6$ 、 $0.03 \leq y \leq 0.3$ 及び $0 \leq z \leq 0.04$ にあるのが好ましいが、このx、y及びzがそれぞれ $0.4 < x \leq 0.6$ 、 $0.075 \leq y \leq 0.225$ 及び $0 \leq z < 0.025$ にある時、特に、得られる蛍光体の経時的な発光輝度並びに発光色の変化の、より少ない蛍光体得られるので好ましい。なお、蛍光体中のEuの濃度（y）は、これが増すと、蛍光ランプ製造時のベークン工程における熱による劣化が大きくなる傾向があるので、Euの濃度（y値）は0.3以下とするのが望ましい。

【0015】これらの蛍光体を蛍光ランプの発光組成物の青色発光成分蛍光体として使用した場合、従来の蛍光ランプの青色発光蛍光体として使用されているEu²⁺、Mn²⁺共付活バリウム・ストロンチウム・マグネシウムアルミン酸塩蛍光体を使用した場合より、高演色、高効率で、かつ経時劣化の少ない蛍光ランプを提供することが可能となる。

【0016】図1は本発明のEu²⁺付活アルカリ土類アルミン酸塩蛍光体及び従来のEu²⁺付活アルカリ土類アルミン酸塩蛍光体をそれぞれ253.7nmの紫外線で励起した時の発光スペクトルを例示するものであり、図1の曲線a及びbはそれぞれ本発明の蛍光体の1例である、Eu²⁺付活バリウム・ストロンチウム・マグネシウムアルミン酸塩蛍光体（ $Ba_{0.4}Sr_{0.5}Eu_{0.1}MgAl_{10}O_{17}$ ）及び従来の蛍光ランプの青色発光蛍光体として使用されているEu²⁺付活バリウム・マグネシウムアルミン酸塩蛍光体（ $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ ）について示したものである。

【0017】図1の曲線a及びbの比較からわかるように、従来のバリウム・マグネシウムアルミン酸塩蛍光体のバリウムの一部をストロンチウムで置換することによって（図1の曲線a）、従来のバリウム・マグネシウムアルミン酸塩蛍光体（図1の曲線b）に比べてEu²⁺に起因する発光のピーク位置が、長波長側に移動するとともに、460～600nmの発光強度が大きくなる。

【0018】また、図2の曲線a及び曲線bは、それぞれ本発明の別のEu²⁺付活アルカリ土類アルミン酸塩蛍光体である、Eu²⁺とMn²⁺とで共付活したバリウム・ストロンチウム・マグネシウムアルミン酸塩蛍光体(Ba_{0.4}Sr_{0.5}Eu_{0.1}Mg_{0.998}Mn_{0.012}Al₁₀O₁₇)及び従来の蛍光ランプの青色発光蛍光体として使用されている、Eu²⁺とMn²⁺とで共付活したバリウム・ストロンチウム・マグネシウムアルミン酸塩蛍光体(Ba_{0.6}Sr_{0.3}Eu_{0.1}Mg_{0.998}Mn_{0.012}Al₁₀O₁₇)をそれぞれ253.7nmの紫外線で励起した時の発光スペクトルを例示するものである。

【0019】図2の曲線a及びbの比較からわかるように、従来のEu²⁺及びMn²⁺で共付活したバリウム・ストロンチウム・マグネシウムアルミン酸塩蛍光体(図2の曲線b)に比べ本発明のEu²⁺及びMn²⁺で共付活したバリウム・ストロンチウム・マグネシウムアルミン酸塩蛍光体(図2の曲線a)はSrによる置換の量を多くすることによってEu²⁺に起因する発光のピーク位置が長波長側に移動するとともに、Mn²⁺に起因する発光ピークの位置は変わらないものの、460~600nmの発光強度が大きくなるためにEu²⁺に起因する発光のピークに対しての相対強度が高くなる。

【0020】このように、本発明のアルカリ土類アルミン酸塩蛍光体はEu²⁺に起因する発光のピーク位置が長波長側に移動し、さらに460~600nmの発光強度が大きくなる。このことは本発明のEu²⁺、Mn²⁺共付活バリウム・ストロンチウム・マグネシウムアルミン酸塩蛍光体は、従来の蛍光ランプの青色発光蛍光体として使用されるEu²⁺、Mn²⁺共付活バリウム・ストロンチウム・マグネシウムアルミン酸塩蛍光体より、MgのMnへの置換量が少なくても、あるいはこの置換量が0であっても、253.7nmの紫外線で励起した時の発光スペクトルにおいて515nmのMn²⁺に起因する発光ピークを含む460~600nmの発光の相対強度を同等にすることができることを意味する。

【0021】本発明のEu²⁺又はEu²⁺とMn²⁺とで共付活されたアルカリ土類アルミン酸塩蛍光体は高輝度で、従来のアルカリ土類アルミン酸塩蛍光体に較べて特に熱による発光効率の低下を抑制し、経時的な発光色の*

(実施例1)

BaCO ₃	0.4	mol
SrCO ₃	0.5	mol
Eu ₂ O ₃	0.05	mol
3MgCO ₃ ・Mg(OH) ₂	0.245	mol
MnO ₂	0.02	mol
γタイプ-Al ₂ O ₃	5.0	mol
AlF ₃ (フラックス)	0.010	mol

上記原料を十分に混合し、増埴に充填し、さらに黒鉛の塊を原料の上に乗せ、蓋をして窒素と少量の水素との混合ガスを通しながら最高温度1450℃で昇降温時間※50

*変動を低減する等の特性改善がなされるが、その理由は、蛍光体母体結晶中のBaの一部をSrで部置換することにより、結晶中におけるBa-O層内の酸素の位置が安定化したためと考えられる。

【0022】一方、本発明の蛍光ランプは上記の本発明のEu²⁺付活又はEu²⁺とMn²⁺とで共付活されたアルカリ土類アルミン酸塩蛍光体を青色発光蛍光体とし、これに例えば赤色発光のY_{2-x}Eu_xO₃(但し、xは0.02≤x≤0.1の条件を満たす数である)で示されるユーロピウム付活酸化イットリウム蛍光体(以下、「YOX蛍光体」という)と、緑色発光のLa_{1-y-z}Ce_yTb_zPO₄(但し、y及びzはそれぞれ0.1≤y≤0.6及び0.1≤z≤0.3の条件を満たす数である)で示されるセリウム及びテルビウム共付活燐酸ランタン蛍光体(以下「LAP蛍光体」という)とを所定の量比で混合した混合蛍光体をバインダーとともに混合して蛍光体スラリーとし、これをガラス管の内壁に塗布した後、一般に知られている方法で蛍光ランプを製造することによって、高演色、高効率で、かつ劣化の少ない蛍光ランプを提供できる。本発明の蛍光ランプにおける青色発光蛍光体(アルミン酸塩蛍光体)と赤色発光蛍光体(YOX)と緑色発光蛍光体(LAP)との混合重量比は得られた蛍光ランプの所望の色温度によって異なるが、発光させた時、白色といえる範囲の発光を呈するためには、青色蛍光体:赤色蛍光体:緑色蛍光体の各混合重量比が、1:0.5~2.5:0.3~3.0の範囲にあれば良く、特に演色度を高めるには色温度が4000~8000K程度を想定して、3色蛍光体の混合量のバランスのとれた、1:0.7~2.0:0.3~3.0の範囲とすることが好ましい。

【0023】なお、本発明のアルカリ土類蛍光体はBaの一部をSrで置換するが、その時のSrの置換量(x)を増し、0.4≤x≤0.6の置換範囲とすることによって、この蛍光体を用いて蛍光ランプを製造する際、ベーキング工程における熱による劣化が小さくなるという効果も有し、高効率な蛍光ランプを提供することが可能となる。

【0024】

【実施例】

※を含めて24時間かけて焼成した。次いで、焼成粉を分散、洗浄、乾燥、篩分の処理を行い、実施例1のEu²⁺、Mn²⁺共付活のバリウム・ストロンチウム・マグ

ネシウムアルミン酸塩青色発光蛍光体 ($\text{Ba}_{0.4}\text{Sr}_{0.5}\text{Eu}_{0.1}\text{Mg}_{0.98}\text{Mn}_{0.02}\text{Al}_{10}\text{O}_{17}$) を得た。

【0025】このようにして得た実施例1の青色発光蛍光体を253.7nmの紫外線で励起した時の発光色は、発光波長ピークが460nmで、発光色度点が $x=0.143$ 、 $y=0.187$ の青色発光を示した。この青色蛍光体を空気雰囲気中で最高温度650℃で15分間熱処理し、その後室温まで冷却した後に253.7nmの紫外線で励起したところ、熱処理前に対する熱処理後の発光効率の比率(熱処理時の輝度維持率)は98.8%であり、ベーキング処理に対する耐熱履歴性が極めて良好であることが分かった。

(比較例1)

BaCO_3	0.6	mol
SrCO_3	0.3	mol
Eu_2O_3	0.05	mol
$3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$	0.245	mol
MnO_2	0.02	mol
γ タイプ- Al_2O_3	5.0	mol
AlF_3 (フラックス)	0.010	mol

蛍光体原料として上記の原料を用いた以外は実施例1の青色発光蛍光体と同様にして比較例1の Eu^{2+} 及び Mn^{2+} 共付活バリウム・ストロンチウム・マグネシウムアルミン酸塩青色発光蛍光体 ($\text{Ba}_{0.6}\text{Sr}_{0.3}\text{Eu}_{0.1}\text{Mg}_{0.98}\text{Mn}_{0.02}\text{Al}_{10}\text{O}_{17}$) を得た。

【0028】このようにして得た比較例1の青色発光蛍光体を253.7nmの紫外線で励起した時の発光色は、発光波長ピークが450nmで、発光色度点が $x=0.144$ 、 $y=0.153$ の青色発光を示した。この蛍光体を実施例1と同様に熱処理した時の、熱処理前に対する熱処理後の発光効率の比率(熱処理時の輝度維持率)を求めたところ、85.5%であり、ベーキング処理に対する耐熱履歴性が悪かった。

【0029】さらにまた、この青色蛍光体を用いて実施例1と同様にして青色単色発光の蛍光ランプ(FL20S)を製造し、実施例1と同様にして1000時間点灯した後、蛍光体をランプの管壁から剥がし、253.7nmの紫外線で励起したときの発光色(X' , Y')は $x'=0.145$ 、 $y'=0.155$ であって、この蛍光体をランプとして使用する前後における蛍光体の発光色度点の差(Δx , Δy)は $\Delta x=0.001$ 、 $\Delta y=0.002$ であった。

【0030】表1及び表2に実施例1及び比較例1の青色発光蛍光体の蛍光体組成、及び、前記蛍光体の発光色(発光ピーク波長、発光色度点①色(x , y))、熱処理前に対する熱処理後の発光効率の比率(熱処理時の輝度維持率)、この蛍光体をランプの蛍光膜として用いた蛍

*【0026】次に、この青色蛍光体をガラスバルブ内面に塗布し、青色の単色発光の蛍光ランプ(FL20S)を製造し、これを1000時間点灯した後、蛍光体をランプの管壁から剥がし、253.7nmの紫外線で励起したときの発光色(X' , Y')は $x'=0.145$ 、 $y'=0.190$ であり、この蛍光体をランプの蛍光膜として使用する前後における蛍光体の発光色度点の差(使用による発光色度の差)は $\Delta x=0.002$ 、 $\Delta y=0.003$ と、使用前後における蛍光体の色度差が極めて小さな値であった。

【0027】

※光ランプを1000時間点灯使用した後、蛍光膜を剥離して回収した蛍光体の発光色度点②(x' , y')、及びランプの蛍光膜として使用する前後における蛍光体の発光色度の差(Δx , Δy)、即ち使用による発光色度の差(②-①)をそれぞれ示した。

【0031】(実施例2~28)実施例1の各蛍光体原料を表1及び表2に示した各組成となるように混合した以外は、実施例1の青色発光蛍光体と同様にして実施例2~28の Eu^{2+} 、 Mn^{2+} 共付活のバリウム・ストロンチウム・マグネシウムアルミン酸塩青色発光蛍光体を製造した。このようにして得た、実施例2~28の各青色発光蛍光体の組成、これらの蛍光体を253.7nmの紫外線で励起した時の発光色(発光ピーク波長、発光色度点①(x , y))、これらの蛍光体を実施例1と同様にして熱処理した時の、熱処理前に対する熱処理後の発光効率の比率(熱処理時の輝度維持率)、これらの各青色蛍光体を用いて実施例1と同様にして青色単色発光の蛍光ランプ(FL20S)をそれぞれ製造し、実施例1と同様にして1000時間点灯した後、蛍光体をランプの管壁から剥がし、253.7nmの紫外線で励起したときの蛍光体の発光色度②(使用後の発光色度点(X' , Y'))、及び使用による蛍光体の発光色度の差(Δx , Δy)、即ち(②-①)をそれぞれ表1及び表2に示した。

【0032】

【表1】

No.	青 色 蛍 光 体 組 成	発 光 色		熱処理時の輝度維持率	使用後の発光色度 (②)		使用による発光色度の差 (②-①)	
		ピーク波長 (nm)	発光色度点 (①)		x'	y'	Δ x	Δ y
実施例 1	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.143 0.187	98.8	0.145	0.190	0.002	0.003
実施例 2	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.145 0.176	96.1	0.147	0.179	0.002	0.003
実施例 3	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.145 0.161	95.8	0.146	0.163	0.001	0.002
実施例 4	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.144 0.145	95.5	0.145	0.147	0.001	0.002
実施例 5	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.146 0.124	97.0	0.147	0.126	0.001	0.002
実施例 6	Ba _{0.4} Sr _{0.5} Eu _{0.1} MgAl ₁₀ O ₁₇	460	0.145 0.114	92.9	0.146	0.116	0.001	0.002
実施例 7	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.975} Mn _{0.025} Al ₁₀ O ₁₇	460	0.145 0.216	98.6	0.146	0.219	0.001	0.003
実施例 8	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.975} Mn _{0.025} Al ₁₀ O ₁₇	460	0.145 0.200	98.9	0.146	0.204	0.001	0.004
実施例 9	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.143 0.186	98.9	0.145	0.189	0.002	0.003
実施例 10	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.146 0.171	98.4	0.147	0.174	0.001	0.003
実施例 11	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.144 0.153	97.8	0.145	0.156	0.001	0.003
実施例 12	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.143 0.138	99.0	0.145	0.141	0.002	0.003
実施例 13	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.97} Mn _{0.03} Al ₁₀ O ₁₇	460	0.143 0.118	96.9	0.144	0.121	0.001	0.003
実施例 14	Ba _{0.4} Sr _{0.5} Eu _{0.1} MgAl ₁₀ O ₁₇	460	0.145 0.104	95.5	0.146	0.106	0.001	0.002
実施例 15	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.975} Mn _{0.025} Al ₁₀ O ₁₇	455	0.144 0.202	97.9	0.146	0.206	0.002	0.004

【0033】

* * 【表2】

No.	青 色 蛍 光 体 組 成	発 光 色 色		熱処理時の輝度維持率	使用後の発光色度 (②)		使用による発光色度の差 (②-①)	
		ピーク波長 (nm)	発光色度点 (①)		x'	y'	Δ x	Δ y
実施例16	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	455	0.144 0.179	99.1	0.146	0.183	0.002	0.004
実施例17	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	455	0.144 0.165	98.5	0.145	0.168	0.001	0.003
実施例18	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	455	0.145 0.149	97.9	0.147	0.152	0.002	0.003
実施例19	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	455	0.145 0.134	97.2	0.146	0.136	0.001	0.002
実施例20	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.97} Mn _{0.03} Al ₁₀ O ₁₇	455	0.146 0.11	98.4	0.148	0.113	0.002	0.003
実施例21	Ba _{0.4} Sr _{0.5} Eu _{0.1} MgAl ₁₀ O ₁₇	460	0.145 0.102	96.9	0.147	0.104	0.002	0.002
比較例22	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.975} Mn _{0.025} Al ₁₀ O ₁₇	460	0.147 0.214	97.5	0.148	0.216	0.001	0.002
実施例23	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.147 0.203	98.2	0.148	0.205	0.001	0.002
実施例24	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	450	0.147 0.187	97.9	0.148	0.189	0.001	0.002
実施例25	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.148 0.172	97.8	0.149	0.174	0.001	0.002
実施例26	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	460	0.147 0.156	97.2	0.148	0.158	0.001	0.002
実施例27	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.97} Mn _{0.03} Al ₁₀ O ₁₇	460	0.146 0.137	97.6	0.147	0.139	0.001	0.002
実施例28	Ba _{0.4} Sr _{0.5} Eu _{0.1} MgAl ₁₀ O ₁₇	460	0.146 0.128	97.1	0.147	0.13	0.001	0.002
比較例 1	Ba _{0.4} Sr _{0.5} Eu _{0.1} Mg _{0.98} Mn _{0.02} Al ₁₀ O ₁₇	450	0.144 0.153	85.5	0.145	0.155	0.001	0.002

【0034】(実施例29) 実施例1のEu²⁺、Mn²⁺共付活バリウム・ストロンチウム・マグネシウムアルミン酸塩青色発光蛍光体 (Ba_{0.4}Sr_{0.5}Eu_{0.1}Mg_{0.98}Mn_{0.02}Al₁₀O₁₇) を30.6重量%と、組成式がY_{1.92}Eu_{0.08}O₃であるYOX赤色発光蛍光体を37.2重量%、組成式がLa_{0.55}Ce_{0.30}Tb_{0.15}PO₄であるLAP緑色発光蛍光体を32.2重量%を、酢酸ブチルにニトロセルロースのラッカーと共に充分に混合して蛍光体スラリーを作製し、ガラス管に塗布して乾燥した後、通常の方法で実施例29の、色温度5000※50

※Kである3波長蛍光ランプ (FL20S) を製造した。このようにして得た蛍光ランプの初期特性は、下記の比較例2の蛍光ランプのランプ光束を100とした時の相対値で99.5であり、また、平均演色性指数Raは90.1であった(表3)。

【0035】(比較例2) 比較のために、青色蛍光体として上記実施例1の青色蛍光体に代えて比較例1のEu²⁺及びMn²⁺共付活バリウム・ストロンチウム・マグネシウムアルミン酸塩青色発光蛍光体 (Ba_{0.6}Sr_{0.3}Eu_{0.1}Mg_{0.98}Mn_{0.02}Al₁₀O₁₇) を用い、各色蛍

光体の混合重量比を表3の通りとした以外は上記の実施例29の3波長蛍光ランプと同様にして比較例2の3波長蛍光ランプ（FL20S）を製造した。これら、実施例29及び比較例2の3波長蛍光ランプの点灯直後における光束の相対値及び平均演色性指数Raを表3に示した。

【0036】（実施例30～56）また、実施例2～28の各青色蛍光蛍光体、実施例29で用いたLAP緑色*

* 発光蛍光体及びYOX赤色蛍光蛍光体をそれぞれ表2に示した混合重量比で混合した混合蛍光体を用いた以外は、実施例29の蛍光ランプと同様にして実施例30～56の3波長蛍光ランプを製造した。得られた各蛍光ランプの点灯直後における光束の相対値、及び平均演色性指数Raを測定して表3に示した。

【0037】

【表3】

実施例 (比較例)	各色蛍光体とその混合比 (重量%)			光 束 (相対値)	平均演色 指数 (R a)
	実施例1の 青色蛍光体	Y O X 赤色蛍光体	L A P 緑色蛍光体		
実施例29	30.6	37.2	32.2	99.5	90.1
実施例30	29.3	36.9	33.8	100.4	90.4
実施例31	28.3	36.1	35.6	100.7	90.4
実施例32	27.3	35.2	37.5	101.0	89.9
実施例33	26.1	34.2	39.7	101.3	89.2
実施例34	26.0	33.5	40.5	101.0	88.7
実施例35	32.4	39.4	28.2	99.1	89.5
実施例36	31.1	37.8	31.1	100.0	89.6
実施例37	30.1	37.0	32.9	100.3	89.9
実施例38	28.9	36.1	35.0	100.9	89.9
実施例39	28.0	35.1	36.9	100.9	89.5
実施例40	26.9	34.4	38.7	101.4	89.2
実施例41	25.6	33.5	40.9	101.9	88.3
実施例42	24.7	32.9	42.4	102.0	87.6
実施例43	31.4	38.5	30.1	99.4	89.8
実施例44	30.0	36.9	33.1	99.8	89.7
実施例45	28.8	36.2	35.0	100.4	89.7
実施例46	27.9	35.3	36.8	100.6	89.4
実施例47	26.7	34.6	38.7	101.3	88.9
実施例48	25.7	33.4	40.9	101.2	87.8
実施例49	25.1	33.0	41.9	101.5	87.3
実施例50	32.6	39.0	28.4	99.0	89.7
実施例51	31.4	38.4	30.2	99.6	90.2
実施例52	30.4	37.4	32.2	100.0	90.6
実施例53	29.3	36.6	34.1	100.3	90.9
実施例54	28.0	35.8	36.2	100.9	90.7
実施例55	26.8	34.8	38.4	101.4	90.2
実施例56	26.4	34.3	39.3	101.3	89.8
比較例 2	26.6	35.6	37.8	100.0	88.6

【0038】表3から明らかなように、本発明の蛍光ランプ（実施例29～56）は、同じユーロビウム濃度の青色蛍光体を使用した比較例2の蛍光ランプと比較して、光束はほぼ同じで、平均演色性指数（Ra）が向上しており、演色性がより改善されたか、あるいは平均演色性指数（Ra）がほぼ同等で光束が向上しており発光効率が改善された。特に実施例30～34及び実施例36～40及び実施例45～47及び実施例52～56の蛍光ランプは比較例2の蛍光ランプと比較して、光束および平均演色性指数がともに向上しており、演色性および発光効率がともに改善された。

【0039】また、表中には例示していないが、実施例※50

※29～56の蛍光ランプは比較例2に比べて継続点灯による経時劣化も改善されていることが確認された。これらの中でも、特に実施例29～33及び実施例36～41及び実施例44～48及び実施例51～55の蛍光ランプ点灯中の経時劣化の改善の度合いは比較例2及び実施例34、実施例35、実施例42、実施例43、実施例49、実施例50、実施例56の蛍光ランプに比べて大であった。

【0040】（実施例57～84、比較例3）さらに実施例1～28及び比較例1の各青色蛍光蛍光体、Y O X赤色蛍光蛍光体並びにL A P緑色蛍光蛍光体をそれぞれ表4に記載した重量比で混合してなる混合蛍光体を蛍光

膜として用いる以外は実施例29の蛍光ランプと同様にして、実施例57～84及び比較例3の、色温度6500Kの3波長蛍光ランプ（FL20S）を製造した。このようにして得られた蛍光ランプについて、点灯直後の*

* 初期光束（相対値）および平均演色指数（Ra）を測定した結果を表4に示した。

【0041】

【表4】

実施例 (比較例)	使用した蛍光体種とその混合比(重量%)					光 束 (相対値)	平均演色 指数(Ra)
	青色蛍光体	赤色蛍光体	緑色蛍光体				
実施例57	実施例1	41.4	Y O X	32.6	L A P	26.0	99.3
実施例58	" 2	39.8	"	32.1	"	28.1	100.5
実施例59	" 3	38.4	"	31.0	"	30.6	101.0
実施例60	" 4	37.1	"	29.7	"	33.2	101.4
実施例61	" 5	35.5	"	28.3	"	36.2	101.8
実施例62	" 6	35.2	"	27.5	"	37.3	101.4
実施例63	" 7	43.7	"	35.6	"	20.7	98.8
実施例64	" 8	42.0	"	33.5	"	24.5	100.0
実施例65	" 9	40.7	"	32.4	"	26.9	100.3
実施例66	" 10	39.1	"	31.2	"	29.7	101.2
実施例67	" 11	37.9	"	29.7	"	32.4	101.2
実施例68	" 12	36.5	"	28.7	"	34.8	101.8
実施例69	" 13	34.8	"	27.6	"	37.6	102.5
実施例70	" 14	33.6	"	26.7	"	39.7	102.7
実施例71	" 15	42.4	"	34.4	"	23.2	99.2
実施例72	" 16	40.5	"	32.2	"	27.3	100.0
実施例73	" 17	39.1	"	31.2	"	29.7	100.6
実施例74	" 18	37.9	"	29.9	"	32.2	100.8
実施例75	" 19	36.3	"	29.0	"	34.7	101.7
実施例76	" 20	34.9	"	27.2	"	37.9	101.7
実施例77	" 21	34.2	"	26.7	"	39.1	102.1
実施例78	" 22	44.0	"	35.0	"	21.0	98.7
実施例79	" 23	42.5	"	34.2	"	23.3	99.6
実施例80	" 24	41.1	"	32.8	"	26.1	100.0
実施例81	" 25	39.7	"	31.7	"	28.6	100.5
実施例82	" 26	38.0	"	30.6	"	31.4	101.2
実施例83	" 27	36.4	"	29.3	"	34.3	101.9
実施例84	" 28	35.9	"	28.5	"	35.6	101.8
比較例2	比較例1	36.2	"	30.2	"	33.6	100.0

【0042】表4から明らかなように、本発明の蛍光ランプ（実施例57～84）は、同じユーロビウム濃度の青色蛍光体を使用した比較例3の蛍光ランプと比較して、光束はほぼ同じで、かつ平均演色性指数（Ra）が向上しており、演色性がより改善されたか、又は平均演色性指数（Ra）がほぼ同等のもので、光束が向上しており、発光効率が改善された。特に実施例58～62及び実施例65～69及び実施例72～76及び実施例80～84の蛍光ランプは、比較例3の蛍光ランプと比較して、光束及び平均演色性指数Raがともに向上し、演色性及び発光効率もともに改善された。

【0043】（実施例85、比較例4）実施例1と同様にして、実施例85の青色蛍光体（Ba_{0.3} Sr_{0.5} Eu_{0.2} Mg_{0.98} Mn_{0.02} Al₁₀ O₁₇）及び比較例4の青色蛍光体（Ba_{0.7} Sr_{0.1} Eu_{0.2} Mg_{0.986} Mn_{0.014} Al₁₀ O₁₇）を製造した。このようにして得た実※50

※実施例85及び比較例4の青色蛍光体の組成、発光ピーク波長、及び発光色度D（x, y）を表5に示した。

【0044】次に、実施例85の青色蛍光体及び比較例4の青色蛍光体（前記蛍光体組成、発光ピーク波長及び発光色度点は表5に示した）を、Y O X赤色蛍光体及びL A P緑色蛍光体と、表6に示した混合割合で混合して混合蛍光体を調製し、実施例29と同様にして実施例85及び比較例4の蛍光体について、色温度5000K、FL20Sの3波長域発光形蛍光ランプを作製した。得られた各蛍光ランプについて、蛍光膜として用いた各色蛍光体の混合割合（重量%）、得られた蛍光ランプの初期光束（相対値）及び平均演色指数（Ra）を測定し、結果を表6に示した。

【0045】

【表5】

No.	青 色 発 光 螢 光 体				
	螢 光 体 組 成	ピーク 波長 (nm)	発光色度点		
			x	y	
実施例57	Ba ₂ Sr ₂ Ba ₂ Mg ₂ Mn _{0.02} Al ₁₀ O ₁₇	460	0.142	0.222	
比較例 3	Ba ₂ Sr ₂ Ba ₂ Mg ₂ Mn _{0.014} Al ₁₀ O ₁₇	455	0.142	0.169	

【0046】

* * 【表6】

No.	螢 光 ラ ン プ				初期光束 (相対値)	平均演色 係數 (R _a)
	螢光体種と混合比 (重量%)					
	青色螢光体	赤色螢光体	緑色螢光体			
実施例 57	実施例 57 螢光体 32.2	Y O X 39.4	L A P 28.4	100.3	92.1	
比較例 3	比較例 4 螢光体 28.0	Y O X 35.9	L A P 36.1	100.0	89.1	

【0047】表6から明らかなように、実施例85の本発明の蛍光ランプは、同じユーロピウム濃度の青色螢光体を使用した、比較例4の蛍光ランプと比較して、光束は高くかつ平均演色性指数(Ra)が向上しており、演色性および発光効率がともに改善された。

【0048】

【発明の効果】本発明は、上記の構成を採用することにより、従来のEu及びMn共付のアルカリ土類アルミン酸塩螢光体に較べて253.7nmの紫外線で励起した時の発光スペクトルにおいてユーロピウムに起因する発光のピーク位置が長波長側に移動し、さらに460～600nmの発光強度が大きくなるもので、特に3波長蛍光ランプの青色発光成分の螢光体として使用した場合※

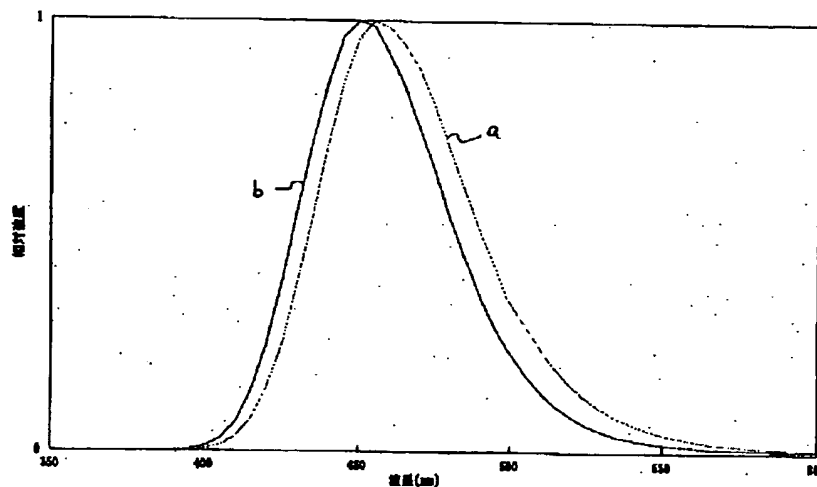
※合、高演色、高効率でかつランプ点灯中の発光色の変化および経時劣化の少ない3波長域発光形蛍光ランプを提供できるようになった。

【図面の簡単な説明】

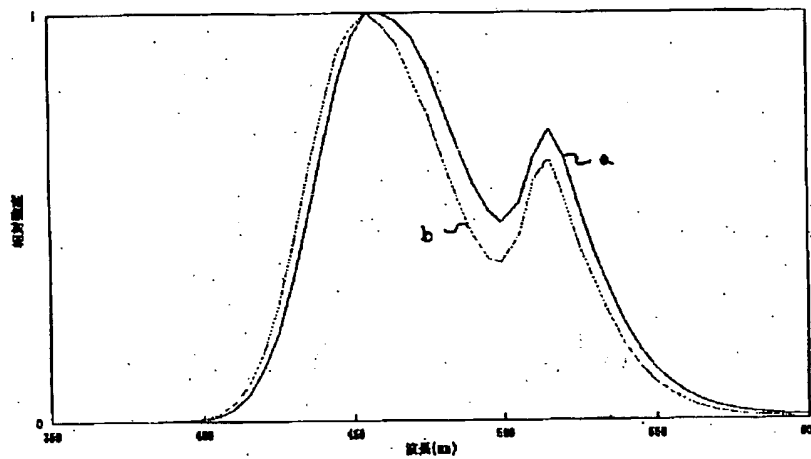
【図1】本発明の一組成のアルカリ土類アルミン酸塩螢光体並びに従来のアルカリ土類アルミン酸塩螢光体を253.7nmの紫外線で励起した時の発光スペクトルを示した図である。

【図2】本発明の別の組成のアルカリ土類アルミン酸塩螢光体並びに従来のアルカリ土類アルミン酸塩螢光体を253.7nmの紫外線で励起した時の光スペクトルを示した図である。

【図1】



【図2】



フロントページの続き

Fターム(参考) 4H001 CA07 XA08 XA12 XA13 XA38
XA56 YA25 YA63
5C043 AA01 AA02 AA03 AA05 CC08
DD28 EA19 EB04 EC20